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Trace metal geochemistry of Walker, Mono, and Great Salt Lakes

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Abstract—Recent sediments were collected from three Basin and Range closed basin lakes (Walker Lake, NV, Mono Lake, CA, and Great Salt Lake, UT) to evaluate the response of a suite of trace metals (Fe, Mn, Cu, Pb, Zn, Cd, Co, Mo, V) to diagenetic processes and assess reactivity, mobility, mineral transformations and precipitation, and organic complexation. Sediments and pore fluids, representing up to 1000 years of deposition, were analyzed for brine and metal composition, pH, alkalinity, and H_2S. Sequential extractions of metals from solids were valuable in locating core horizons where metals are mobilized or precipitated and in the interpretation of pore-fluid metal profiles. Sedimentary metals initially associated with Fe-Mn oxides and organic matter respond to changes in biologically induced redox conditions by forming sulfide solids and humic acid complexes. Walker Lake metals are tightly bound near the sediment-water interface by oxides which only slowly dissolve in the anoxic sediments. At 50–60 cm of sediment depth, dissolution of oxides results in the most extensive metal redistribution. At Great Salt Lake sedimenting particles are entrained within the dense bottom brines where maximum organic decomposition and H_2S production occurs. Pyrite formation occurs very close to the sediment-water interface and renders most metals (Mo, V, and Cd excluded) insoluble except to hot concentrated acids. Mono Lake metals show maximum reactivity to extracting solutions just below the sediment-water interface. Very high pore-fluid sulfide levels (0.02 M) immobilize metals through the formation of metastable Fe monosulfides but metal reactivity is high as pyrite formation is hindered in the high pH environment. The Great Salt Lake is the only system where metal immobilization, through the formation of pyrite, was observed to have gone to completion.

INTRODUCTION

THE FATE of trace metals in sedimentary basins is dependent on the speciation of the metals during deposition and subsequent reactions during diagenesis. Previous work (JENNE, 1977, TUREKIAN, 1977, BALISTRIERI and MURRAY, 1981, 1982, 1983, 1984) has shown that trace metals, in oxygenated low temperature environments, are associated with reactive particles such as amorphous to crystalline oxides of Fe and Mn, organic coatings on suspended particles, and biological material. More recent work (JACOBS *et al.*, 1985; BOULEGUE *et al.*, 1982; LORD and CHURCH, 1983; KREMLING 1983; LUTHER *et al.*, 1982) has been directed towards the chemistry of trace metals across redox boundaries where the reductive dissolution of metal oxides and anaerobic degradation of organic matter is occurring. The release of trace metals to brines occurs during these processes. The major problems affecting trace metals in these environments include solute speciation with respect to chloride, bisulfide, polysulfide, and dissolved organic ligands, and the nature of the solid phases controlling metal solubility. It has been suggested that trace metals are not in equilibrium with pure metal sulfides during low temperature diagenesis but instead are involved in co-precipitation reactions, possibly with Fe sulfides (JACOBS *et al.*, 1985). It is necessary to understand the solid phase associations of trace metals and the dissolved speciation so that thermodynamic models of metal redistribution and ore-forming processes can be formulated.

This study examines the solution and solid phase chemistry of Fe, Mn, Cu, Pb, Zn, Co, Cd, Mo, and V in the lake waters and Recent sediments of closed basin lakes of the Basin and Range province. Two alkaline ($Na\text{-}CO_3\text{-}Cl\text{-}SO_4$) systems, Walker Lake, NV, and Mono Lake, CA, and one non-alkaline ($Na\text{-}Mg\text{-}Cl\text{-}SO_4$) system, Great Salt Lake, UT, were studied. These lakes offer unique opportunities for investigating the effects of brine composition and evolution on redox chemistry, organic matter diagenesis, and sulfide precipitation, and their influence on trace metal distribution. Both Mono and the Great Salt Lake were chemically stratified with anoxic bottom waters during this study whereas

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Walker Lake was not stratified and had an oxygenated sediment-water interface. Alkaline lake basins have been proposed by EUGSTER (1985) as potential sites of ore forming processes. In addition, the processes occurring here can be contrasted with the more widely studied marine systems. This study examines the initial reactions occurring during trace metal deposition.

STUDY AREA

The lakes chosen for this study lie within the Basin and Range physiographic province of North America. Field work took place during the summers of 1984, 1985, and 1986. The area is characterized by north-south trending mountain ranges many of which are bounded by fault scarps. The ranges are separated by valleys which are filled with Cenozoic continental deposits. The lakes are perennial closed basin systems with no drainage outlets. They are remnants of much larger glacial lakes which had very high stands during the Pleistocene. A map of the present lakes and Pleistocene basins is shown in Fig. 1. The lake level chronology for these basins has been reported by BENSON (1978), THOMPSON *et al.* (1986), BENSON and THOMPSON (1987), BRADBURY *et al.* (1988), and SPENCER *et al.* (1984). These studies have shown that a rapid drop in lake level affected all three basins about 13,000 years ago in response to waning glacial climates.

Walker Lake

Walker Lake is one of the remnants of pluvial Lake Lahontan. It is bounded by the Wassuk Range on the west and the Gillis Range on the east. The Wassuk Range is composed of volcanic and granitic rocks whereas the Gillis Range is composed of intermediate to felsic Triassic volcanics and Mesozoic granitic rocks. The Walker River is the major source of fresh water with the drainage originating within the Sierra Nevada Mountains. The inflow water has carbonate alkalinity exceeding the concentration of alkaline earth ions. Evaporative concentration leads to a Na-CO_3-Cl-SO_4 brine composition (EUGSTER and HARDIE, 1978). The lake is at an early stage of brine evolution; its ionic strength is 0.17 and its pH is 9.2. The lake is monomictic, with a fall overturn following summer thermal stratification.

Evidence for past desiccation or extreme low stands of Walker Lake are recorded in the pore fluids. A region designated as the zone of salt flux (SPENCER, 1977) is shown on the map in Fig. 2a. This is the hydrographic low of the basin where concentrated brines and/or salts were deposited. A diffusive flux of these dissolved salts supplies solutes to the modern lake. The most recent desiccation or extreme low stand ended about 2500 years ago (BRADBURY *et al.,* 1988). The lake filled rapidly after this time to close to the present level. The desiccation may have been related to either climatic factors or diversion of the Walker River. Two sampling sites were chosen for Walker Lake and their locations are shown in Fig. 2a. Site WL2, at 34.5 m of depth, is at the hydrographic low, within the area of salt flux. Site WL1, at 33 m of depth, is outside of the area of salt flux.

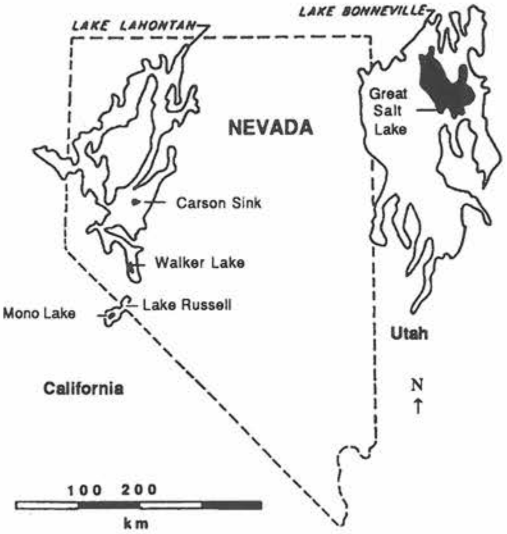


FIG. 1. Study area map showing locations of present lakes and Pleistocene precursors.

Mono Lake

Mono Lake is the modern remnant of pluvial Lake Russell and is located at the base of the east facing escarpment of the Sierra Nevada Mountains. Three sides of the lake are flanked by Cenozoic volcanics. Metasedimentary rocks, lower Paleozoic in age, which were intruded by Mesozoic plutonic rocks are found on the western side. Changes in historic lake levels before 1940 reflect the general nature of drought and wet periods. Currently, the lake is severely affected by diversion of inflow streams to the Los Angeles Aqueduct. The lake level has fallen over 12 m since diversion began in 1941. A 2.5 meter rise in lake level occurred in the early 1980's in response to two winters with heavy precipitation (Los Angeles Department of Water and Power Briefing Document, March, 1984). The influx in fresh water resulted in chemical stratification of the water column. The stratification broke down

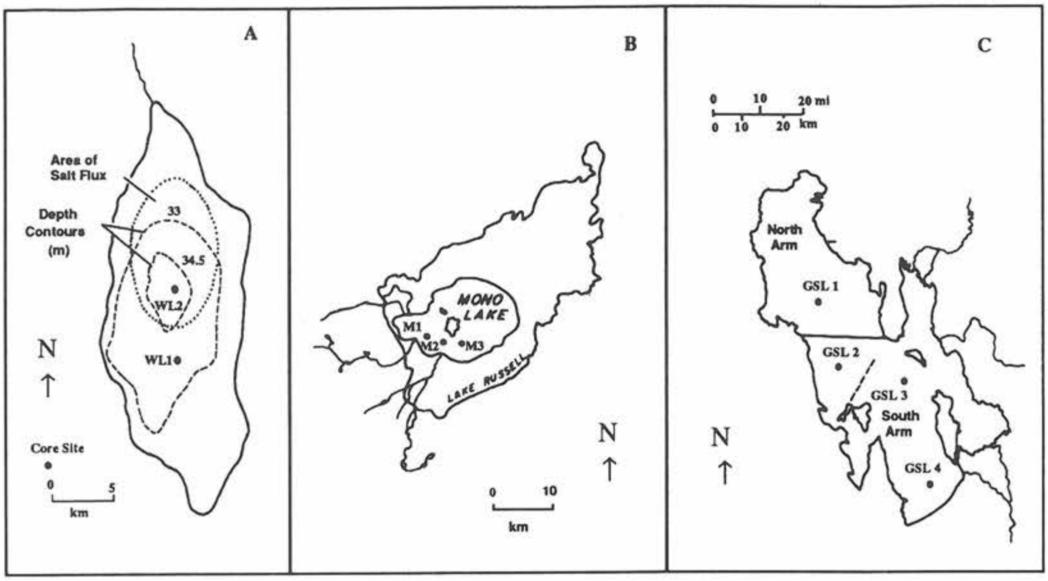


FIG. 2. Locations of sample sites and lake morphology: a) Walker Lake; b) Mono Lake; c) Great Salt Lake: The dashed line marks the location of a sub-aqueous carbonate ridge. The solid line marks the location of the railroad causeway.

and the entire water column mixed in November, 1988 in response to two consecutive drought years (A. MAEST, personal communication, 1989).

The inflow to Mono Lake is Sierra Nevada streams. The inflow water has carbonate alkalinity in excess of the concentration of alkaline earths, so a Na-CO_3-Cl-SO_4 brine forms upon evaporative concentration. Mono Lake waters are in an advanced state of brine evolution; its pH is 9.65. Three sampling sites were chosen for sediment coring (Fig. 2b). They are located in a region of a thick accumulation of mud as reported in a study of Mono Lake bathymetry (SCHOLL *et al.*, 1967). The water depths range from 30 to 33 m.

Great Salt Lake

The Great Salt Lake is the modern remnant of pluvial Lake Bonneville. The lake occupies three interconnecting fault bounded depressions or grabens which are flanked by two parallel horsts and crossed by two other discontinuous and partly submerged horsts (STOKES, 1980).

The lake has been divided into a North and South Arm by a railroad causeway. In addition, a subaqueous carbonate ridge separates the lake into a North and South Basin (SPENCER *et al.*, 1984) (Fig. 2c). Three rivers supply most of the dilute input with all of the inflow occurring in the South Arm. The North Arm receives water from rain, runoff and a few hydrothermal springs. Brine concentrations differ in the two arms of the lake; the most concentrated waters occur in the North Arm. The South Arm is chemically stratified with the most concentrated brines occurring in the bottom waters of the North Basin region of the South Arm. In addition, a deep brine occurs in the southern basin of the lake. Sampling sites, shown in Fig. 2c, were chosen to coincide with these brine bodies. Coring was attempted but was not possible in the North Arm due to a layer of halite at the sediment-water interface. The successful sampling locations include one North Basin site and two South Basin sites. The southernmost site will hereafter be referred to as the South Basin deep site, after SPENCER (1982) and SPENCER *et al.* (1985), to distinguish it from the more northerly South Basin site. The water depths ranged from 12.5 to 13 m.

The concentration of alkaline earths, of the inflow water, is close to the amount of carbonate alkalinity. Neither calcium nor carbonate species increase in concentration during evaporative concentration. The resulting brine is a Na-Mg-Cl-SO_4 system with low buffer capacity relative to Walker and Mono Lakes.

METHODS

Field work

Lake water samples were obtained with a plastic Kemmerer type sampler. Temperature was measured on sample splits with an Orion temperature probe. Water samples were then placed in polyethylene bottles and stored on ice until filtration. All sample bottles were cleaned by soaking for several days in a 0.2 N solution of Ultrapure nitric and hydrochloric acid (Alfa Chemical Co.) followed by rinsing with ultrapure water from a Millipore water system. Samples were also taken, with the water sampler, for pH, alkalinity, and sulfide measurements. The remaining water was filtered through all plastic Nuclepore filter holders which had been cleaned by a similar procedure as the sample bottles. The filter holder was equipped with 0.2 micrometer Nuclepore filters and connected to a plastic syringe. For the Great Salt Lake water column 0.45 micrometer Millipore filters were used. Filtered waters from the Great Salt and Walker Lakes were preserved with 65% Ultrapure HNO_3 to a pH between 1 to 2. This was not possible with Mono Lake waters because of the high alkalinity which would require too large a quantity of acid to effect a drop in pH.

Lake sediment samples were collected by two methods. Cores, up to one meter in length, were collected with a gravity corer. This consisted of a cylinder for holding polycarbonate tubing and a plunger which closes on contact with sediment and retains the solids by vacuum. Upon retrieval the cores were capped and stored in an upright position.

Solid sampling of the sediment-water interface was supplemented by the use of an Eckman dredge. Undisturbed samples of the top 20 to 25 cm of sediment were taken from the dredge with either a cut 60 cc syringe, modified to act as a mini piston corer, or with polycarbonate tubing.

Within hours after collection, pore fluids were recovered from the cores. The tubing was cut in 5 to 10 cm sections and teflon filter holders, containing 0.2 micrometer Nuclepore filters, were installed in each end. A squeezing device, which employs a teflon piston, compresses the sediment. This causes fluid to flow through the filters and into tygon tubing with final collection in plastic syringes. The entire squeezing configuration is closed to the atmosphere, excluding any contact with oxygen. This was the same type of pore-fluid squeezer described in SPENCER *et al.* (1985). Subsamples of pore fluid were taken for measurements of pH, alkalinity, and sulfide. The remaining water was placed in polyethylene bottles. Walker and Great Salt Lake pore fluids were acidified to pH 1 to 2 with Ultrapure HNO_3 and the Mono Lake pore fluids were stored at the natural pH (between 9.2 to 9.6). The squeezed sediment was double wrapped in plastic ziplock bags, double wrapped in plastic, and taped shut. The samples were refrigerated until subsequent analyses. The Eckman sub-samples were extruded in two to three cm sections in a nitrogen filled glove bag, and placed in 50 cc centrifuge tubes. The tightly sealed tubes were spun at 5500 rpm. The recovered pore fluid was filtered and saved for metal analyses. The tubes were re-sealed under nitrogen and refrigerated for sequential and humic acid trace metal extractions.

Field analytical methods

The following methods were used on lake and interstitial fluids. pH measurements were made on samples at room temperature (25°C). An Orion Research Model 231 portable pH/mv/temperature meter was used with a combination electrode. The meter was calibrated with pH 7 phosphate and pH 10 carbonate buffers.

Alkalinity titrations, using standardized sulfuric acid, were made on diluted samples from Walker and Mono Lakes and on undiluted samples from the Great Salt Lake using the Orion pH meter. The end-points of the titrations were determined with a Gran plot (STUMM and MORGAN 1981).

The methylene blue method of LINDSAY and BAEDECKER (1988) was used for the determination of total sulfide (H_2S, HS^-, and S^{2-}). An 8 ml water sample, collected in a syringe from the squeezing device, was connected to a three way stopcock along with another syringe containing 2 ml of the spectrophotometric reagents ferric chloride and *N,N,*-dimethyl-*p*-phenylene diamine. After a 20 minute development time in the dark the sample was analyzed, with a spectrophotometer, at 670 nm. Using this colorimetric method, the reagents and spectrophotometer were calibrated in the laboratory with a standardized sulfide solution. In the field, samples of lake water were placed in a syringe soon after collection and analyzed in an identical manner.

Laboratory methods

Brines

Sodium, K, and Mg were analyzed from diluted samples by atomic absorption spectrophotometry. Since the samples were highly diluted, salt matrix affects were reduced, if not eliminated, and concentrations were determined from standard curves. Calcium concentrations tended to be low in the alkaline waters and therefore the samples could not be diluted to avoid matrix effects. As a result, the method of standard additions had to be used for quantification.

Chloride and sulfate were determined on diluted samples using a Dionex Ion Chromatograph with a standard curve prepared from peak area measurements.

Dissolved organic carbon (DOC) was determined with a Dohrman DC-80 Organic Carbon Analyzer. The measurement is based on oxidation of organic carbon to carbon dioxide by ultra-violet light in the presence of potassium persulfate plus oxygen. The evolved CO_2 was analyzed by infra-red detection. Prior to oxidation the sample was acidified and purged with nitrogen to remove dissolved CO_2.

Dissolved Fe, Mn, Mo, V, Co, and Cu were determined by direct injection of diluted samples into graphite tubes for analysis by flameless atomic absorption spectrophotometry using a Perkin-Elmer HGA-500 programmer interfaced to a Perkin-Elmer 4000 atomic absorption spectrophotometer. Quantification was accomplished by the method of standard additions. For the analysis of Mn and Co 50 micrograms of magnesium nitrate were co-injected as a matrix modifier. Fe, Mo, V, and Co were analyzed with standard graphite tubes whereas the L'vov platform type were used for Mn and Cu (SLAVIN *et al.*, 1983). High purity grade argon was used as the purge gas. Background correction was accomplished with either a tungsten or a deuterium lamp, depending on the wavelength. Dissolved Zn was analyzed by flame atomic absorption spectrophotometry. Quantification was by the method of standard additions.

Dissolved Pb and Cd were analyzed by differential pulse anodic stripping voltammetry. The working electrode is a hanging mercury drop and a silver/silver chloride electrode is the reference. The instrument was an EG & G Princeton Applied Research Polarographic Analyzer/Stripping Voltammeter. The plating potential was -1.20 volts. The purging time was 4 minutes followed by a deposition time of 30 seconds and an equilibration time of 15 seconds. The differential pulse height was 50 mv and the anodic scan was from −1.20 volts to +0.15 volts at a rate of 2 mv per second. Data is collected on a chart recorder and quantification is by a standard curve of peak height.

Gel permeation chromatography was used to separate complexed metals from "non-complexed" ions. The eluate from the column was analyzed by flame or flameless atomic absorption spectrophotometry. Complete details of the gel permeation procedure are described in the section on the humic acid bound metal extraction.

Sediment analyses

Total Organic Carbon (TOC). Sediment samples were dried at 70°C in an oven. A 3 to 5 g sample is placed in 10% HCl until all carbonates have dissolved. The sample was then centrifuged, washed with distilled/de-ionized water, re-centrifuged, dried, and weighed. The dry sample is analyzed by combustion on a LECO carbon analyzer. Vanadium pentoxide is added to the sample to aid combustion. The per cent organic carbon is reported relative to a standard and on the dry weight of the sample prior to carbonate removal.

Total sedimentary metals. Fe, Mn, Cu, Zn, Pb, Co, Cd, and Mo analyses were performed by X-Ray Assay Laboratories, Ltd. of Ontario, Canada, employing total acid dissolution of the sediment, followed by flame atomic absorption for quantification. Vanadium was analyzed by a fusion recovery technique.

Aqua regia extractable metals. This is defined for this study as those metals which can be solubilized by treatment with hot aqua regia. This quantity of metal is assumed to be the maximum amount which is subject to re-mobilization by diagenetic processes. The extracting solution is 2.6% Ultrapure nitric acid plus 2.4% Ultrapure hydrochloric acid. A 0.5 g aliquot of oven dried sediment was placed in a polyethylene bottle with 10 ml of aqua regia and baked for one hour at 75°C. The solution was shaken for one hour and filtered through a 0.4 micrometer Nuclepore filter in an all-plastic holder. The sediment was washed with ultrapure water and the wash was filtered, combined with the aqua regia solution and diluted to 25 ml. The metals were analyzed by atomic absorption spectrophotometry.

Sequential extractions. These extractions were performed on aliquots of wet sediment, 2 to 3 g equivalent dry weight, according to the methods of TESSIER *et al.* (1979) with some modifications. The dry weight is determined on a separate aliquot. The sample is placed in a 50 ml centrifuge tube with 20 ml of extraction solution under a nitrogen atmosphere. All extraction solutions, except for hydrogen peroxide, are purged with nitrogen before injection to remove dissolved oxygen. At the end of the extraction step the solution is recovered by centrifugation, the sediment is washed with nitrogen purged ultrapure water, and the wash water is combined with the extraction solution. The extracting steps, times, and chemicals used are as follows: Solution 1. Millipore ultrapure water wash, 15 mls; Solution 2. Neutral cation exchanger, 1 M NH_4CH_3COO, pH = 7.15, prepared from reagent grade ammonium hydroxide (Fisher Scientific) and Ultrapure acetic acid (Alfa Chemical Co.), extraction time = 2 hours; Solution 3. Acidic cation exchanger, 0.5 M $NaCH_3COO$, pH = 4.85, prepared from Ultrapure acetic acid and Ultrapure sodium hydroxide (Alfa Chemical Co.), extraction time = 4 hours; Solution 4. Reducing Solution, 0.5 M hydroxylamine hydrochloride in 0.01 N nitric acid, prepared from 99+% $NH_2OH \cdot HCl$ (Alfa Chemical Co.) and Ultrapure nitric acid (Alfa Chemical Co.), extraction time = 4 hours; Solution 5. Oxidizing Solution, 30% hydrogen peroxide adjusted to pH 2.5 with nitric acid, prepared from reagent grade hydrogen peroxide (Baker Chemical Co.) and Ultrapure nitric acid. 15 ml of solution are introduced to a sample until foaming ceases. This usually takes several days. After oxidation, the sediment is extracted overnight with 0.5 M ammonium acetate, pH = 2.2. This is prepared from Ultrapure acetic acid and Suprapur ammonium chloride (MCB Chemical Co.). The ammonium acetate step is necessary to extract metals which may have adsorbed onto oxidized phases after the peroxide treatment. Analysis of all the extracting solutions showed that they contained less than one part per billion of interferring metals.

The purpose of the selective extraction experiments is to determine what compositions of solutions are capable of mobilizing metals from the sediments. This provides an indication of the strength of metal bonding in the solid phases and may provide some clues as to the solid phase residence of the trace metals. The ultimate goal is to predict metal mobilization and precipitation interactions during diagenesis. Knowledge of detailed solid phase composition is necessary to model metal mobilization thermodynamically. Extractions were carried out on two separate aliquots. A sequential extraction was made of the first aliquot and an extraction for humic acid bound metals was made of the second. Ideally, the neutral exchanger extracts metals from exchangeable positions on clay or other minerals and organic matter, the acidic cation exchanger attacks carbonate minerals, the reducing solution attacks Mn oxides and labile Fe oxides, and the oxidizing solution attacks labile sulfides and labile organic matter. Labile sulfides and organic matter are solids which completely dissolve during the time frame of the experiment.

There has been much discussion of the selectivity and utility of these methods for the interpretation of metal solid phase residence. See, for example JONES and BOWSER (1978), VAN VALIN and MORSE (1982), RETTIG and JONES (1986), and MARTIN *et al.* (1987). The major problems cited include possible dissolution of non-target phases and/or re-adsorption of trace metals by other solids. Since the extractions involve pH and redox changes trace metals may be re-distributed to different solids during the course of the experiment. The peroxide extraction can generate acidity which may mobilize metals. Oxidation of labile metal sulfides will generate protons in a manner analagous to the generation of acid from pyrite-containing mine tailings as described in STUMM and MORGAN (1981). Therefore, more than one possible interpretation may be obtained from extraction data. The extraction results and pore fluid data are used together to interpret the most probable reactions and solid phase compositions affecting trace metal diagenesis for the sedimentary interval under consideration. One core from each lake was chosen for these extractions.

Humic acid bound metals. This extraction is performed on a separate aliquot of sediment. The sample size for Mono and Walker Lakes was 2 to 4 g whereas for the Great Salt Lake up to eleven g, dry weight, were extracted. The wet sediment was placed in 50 ml polycarbonate centrifuge tubes under a nitrogen atmosphere. To this, 20 mls of nitrogen purged 0.1 N Ultrapure NaOH were added and the reaction was allowed to proceed overnight. Both humic and fulvic acids are recovered by this extraction.

The basic extraction may also result in the dissolution of fine clays. The fluid was recovered by centrifugation and all fluid transfers were performed under a nitrogen atmosphere. The extraction was repeated with fresh NaOH. Five extractions were necessary to recover the majority of humic substances. The combined extracts were diluted to a known volume and analyzed for metals. Prior to instrumental analysis an aliquot of the fluid was spun on a high speed Eppendorf microcentrifuge to remove suspended particles.

Gel permeation chromatography was used to separate the humic acid complexed metals from the free metals. The chromatographic medium consisted of a 10 mm internal diameter column packed to a height of 19 cm with Sephadex G-25 packing material, bead size of 50–150 micrometers. The mobile phase consisted of 0.01 M Tris buffer, pH = 8.0. The pH was adjusted with Ultrapure HCl. The buffer was dissolved in 0.01 M Ultrapure NaCl (Alfa Chemical Co.). The elution volume of a nonretained solute, or high molecular weight organic matter, was determined with Blue Dextran (molecular weight = 2,000,000) whereas the elution volume of free metals was determined with standard solutions. The humic acids are colored and their progress through the column can be determined visually. The colored humic acids eluted at the same volume as the Blue Dextran. However, fulvic acids are recovered by the sodium hydroxide extraction along with other organic compounds with a wide variety of molecular weights. There are likely other organic compounds present which elute after the colored material. Therefore, the elution volume of Blue Dextran is used, operationally, to define the separation between metals complexed to high molecular weight organic compounds and uncomplexed metals. Some of the metals eluting after the elution volume of Blue Dextran may also be organically complexed. Chromatographic fractions were collected manually and analyzed by flame or flameless atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Walker Lake brine chemistry

The Walker Lake water column is alkaline, with a pH of 9.2. The concentration of the major elements is given in Table 1. The DOC concentrations of the lake water are moderately high and range from 27 to 30 mg/l. Thermal stratification of the lake waters occurs from late spring to summer with hypolimnetic oxygen depletion occurring during late summer. At all other times of the year oxygen reaches the bottom sediments. A redox gradient occurs very near to the sediment-water interface. Just above the sediment-water interface the pe is presumably controlled by the O_2/H_2O system, at a value near 12 (STUMM and MORGAN, 1981). Just below the sediment-water interface at site WL1, the pe, as calculated from the SO_4^{2-}/HS^- system, is between −4.75 to −5.0. At site WL2, the corresponding pe is −5.1 throughout the core. The water column, with a pH of 9.2, is a favorable environment for the adsorption of cationic trace metals onto Fe oxides and organic matter. The values of pe, from both sites, suggest that Fe and Mn oxides should start dissolving below the sediment-water interface (STUMM and MORGAN, 1981).

Table 1. Composition of Walker Lake water (samples collected: July, 1984)

Species	Concentration (mg/l)
Na^+	3000.0
K^+	153.0
Ca^{2+}	9.4
Mg^{2+}	121.0
Li^+	1.0
Sr^{2+}	2.3
Cl^-	2080.0
SO_4^{2-}	2172.0
F^-	16.5
SiO_2	1.2
Alkalinity as milliequivalents/l:	44.8
pH: 9.2	

The waters are supersaturated with respect to calcite. The saturation index varied from 1.3 near the surface to 1.1 at depth during the summer sampling. For aragonite the saturation index varied from 1.1 near the surface to 1.0 at depth. The primary carbonate mineral accumulating at the sediment-water interface is monohydrocalcite.

The pore-fluid profiles of Na^+, Cl^-, SO_4^{2-}, sulfide, alkalinity, pH, and DOC, shown in Fig. 3, reveal that the two coring locations have different brine compositions. The most concentrated waters occur in the hydrographic low of the basin where brines or salts were deposited during past desiccation events. These brines are now diffusing to the surface. Sulfur chemistry is different at the two sites. Sulfate reduction goes to completion near the bottom of core WL1 but abundant sulfate is present at the bottom of core WL2 from upward diffusion of brines. Sulfide production is affected by sulfate concentrations at the two sites. Sulfide concentration reaches a maximum near the bottom of core WL1. At site WL2 the concentrations are higher and sulfide continues to form past the point of maximum core penetration. The production is limited only by the availability of labile organic matter. The increase in pore-fluid alkalinity, relative to the lake water, at site WL1 is driven by sulfate reduction, whereas at site WL2 the increase is driven by both sulfate reduction and the diffusive flux coming from buried evaporites not present at depth at site WL1. Despite the increases in alkalinity the pore-fluid pH drops at both locations. This is due to the release of carbon dioxide and organic acids from decomposing organic matter. The pH drops

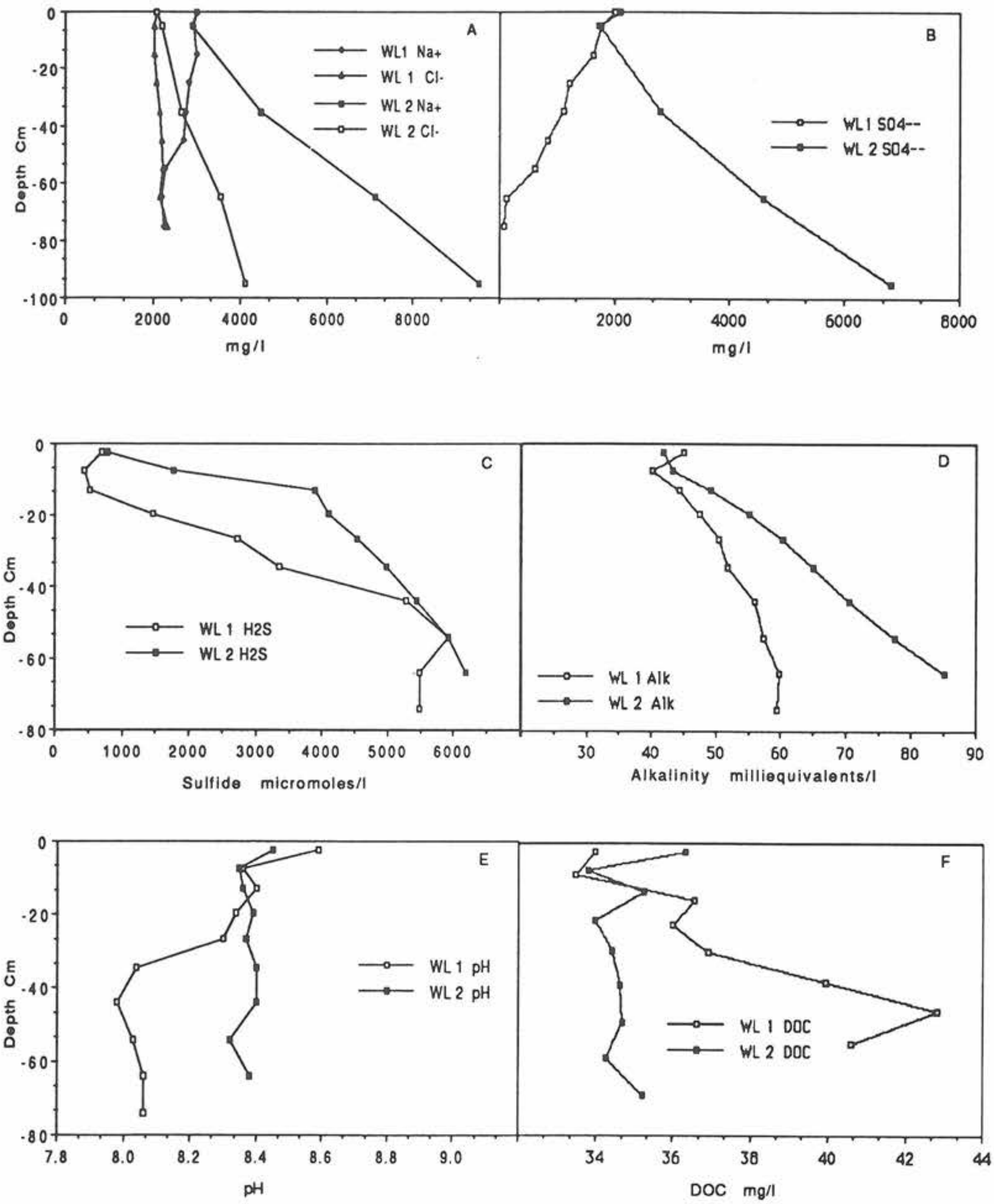


FIG. 3. Walker Lake pore-fluid major element geochemistry: a) Na^+ and Cl^-; b) sulfate; c) sulfide; d) alkalinity; e) pH; f) DOC.

by over one half unit across the sediment-water interface. It is buffered at values near 8.4 at site WL2 and at a value near 8.1 at site WL1. The DOC of the pore fluids increases relative to the water column with concentrations between 34 to 43 mg/l.

The water column metal concentrations are given in Table 2. Fe and Mn concentrations are low which is consistent with the oxygenated conditions. Molybdenum has the highest concentration of all metals. This is due to its presence as molybdate, MoO_4^{2-}, which has high solubility in an oxidizing alkaline brine.

Significant changes in dissolved metal concentrations occur just below the sediment-water interface. The trace metal profiles are shown in Fig. 4. Iron concentrations are higher than the overlying

Table 2. Walker Lake water column. Trace elements and dissolved organic carbon

Depth (m)	Metal concentration: micrograms/liter Dissolved organic carbon concentration: milligrams/liter								
	Fe	Mn	Cu	Zn	Cd	Co	Mo	V	DOC
1.0	2.9	1.7	0.8	41.0	N.A.*	N.D.**	N.A.	7.3	30.5
5.0	N.A.	9.0	N.A.	16.6	1.9	N.D	269	6.7	29.0
15.0	3.7	4.7	0.7	11.3	0.4	0.4	334	8.3	26.7
25.0	5.3	4.7	0.4	10.2	0.4	1.0	321	8.3	27.2

* N.A. Not analyzed.

** N.D. Not detected.

water with the mobilization due, in part, to reductive dissolution of Fe oxide and decomposition of algal debris. The difference in Fe concentrations at the two coring locations could be due to solubility control by sulfide as the two concentrations are inversely correlated, but solubility calculations indicate that Fe is not in equilibrium with pure solid sulfide phases. The ion activity products for the Fe-S system of site WL2 are shown in Fig. 4b. These were calculated with WATEQ4F (BALL *et al.*, 1987). Supersaturation with respect to amorphous Fe sulfide, mackinawite, and pyrite occurs throughout the core.

Mn concentrations increase with depth indicating the presence of a dissolving phase. Copper concentrations are lowest near the sediment-water interface. There is some indication of mobilization in the central region of the core and a trend towards decreasing concentration lower. A mobilization of Zn occurs at 5 to 8 cm below the sediment-water interface. Zn concentrations tend to stabilize below that depth. The Co profiles are substantially different at the two sites with higher concentrations at site WL2. This indicates either a greater rate of Co release from dissolving solids at this site or, alternatively, stabilization of dissolved Co by some ligand. The dissolved Pb profile for site WL2 is considered tentative as this element was analyzed by differential pulse anodic stripping voltammetry and the peak position was shifted in a negative direction from that of the standard. This can occur if the metal is strongly complexed to a ligand. A mobilization of Mo and V is indicated between 10 to 20 cm of core. Both metals tend to decrease in concentration below that depth. Cadmium is undetectable in the pore fluids.

Walker Lake sedimentary chemistry

The mineralogy of Walker Lake sediments has been described by SPENCER (1977). His analyses showed that the sediments are composed of 45 to 49% clay minerals, from 9 to 16% quartz, from 7 to 12% feldspars, and about 20% carbonate minerals. The clay minerals are of the smectite-illite type with smectite dominating. The carbonate mineral which is currently accumulating at Walker Lake is monohydrocalcite. This is a rare mineral which precipitates as trigonal bipyramidal crystals from a gel-like precursor. It is not known what conditions at Walker Lake are responsible for the precipitation of this mineral. SPENCER (1977) showed that it is slowly replaced by low magnesium calcite within the sediments. This forms in response to a drop in the pore-fluid magnesium to calcium ratio. Magnesium is lost from the pore fluids due to uptake by clay minerals (SPENCER, 1977). An Fe-oxide gel is present just under the sediment-water interface. The gel is thin, about 1 to 2 mm thick, and bright red. It probably originates from upward diffusion of reduced Fe which is oxidized and precipitated in the region of higher pore-fluid pe near the sediment-water interface. The gel is of major significance for trace metals as it is freshly precipitated and capable of adsorbing metals out of solution. It is near the sediment-water interface where the pH is close to 9, a favorable environment for trace-metal adsorption (BENJAMIN and LECKIE, 1981).

The concentrations of aqua regia extractable metals and total sedimentary metals are given in Table 3. The profiles for Mo and V are shown in Fig. 5. The shape of these profiles suggest that diagenetic mobilization or re-distribution of these two metals has occurred. These profiles are similar to that described for solid phase Mn in Lake Michigan sediments (ROBBINS and CALLENDER, 1975). A diagenetic model was proposed by those workers to explain this type of re-distribution. The mechanism for this mobilization, in Walker Lake sediments, is discussed later in this paper. The other metals show no apparent sedimentary concentration profiles which could be due to anthropogenic or diagenetic re-distribution for the length of the core. Iron, Mn, Cu, and Zn show somewhat higher concentrations near the bottom of the core. The concentrations of Cu, Zn, Pb, and Co are very close to the values of the "average black shale" of VINE and TOURTELOT (1970). Molybdenum is above this value in the enriched zone whereas V only approaches the value near the enriched zone.

Total sedimentary organic carbon is shown in Fig. 6. The profiles show that concentrations tend to decrease down to the 45 cm horizon with slight increases from 45 to 65 cm. Three horizons (0 to 16 cm, 23 to 35 cm, and 49 to 59 cm) were analyzed for humic acid concentrations. In these horizons,

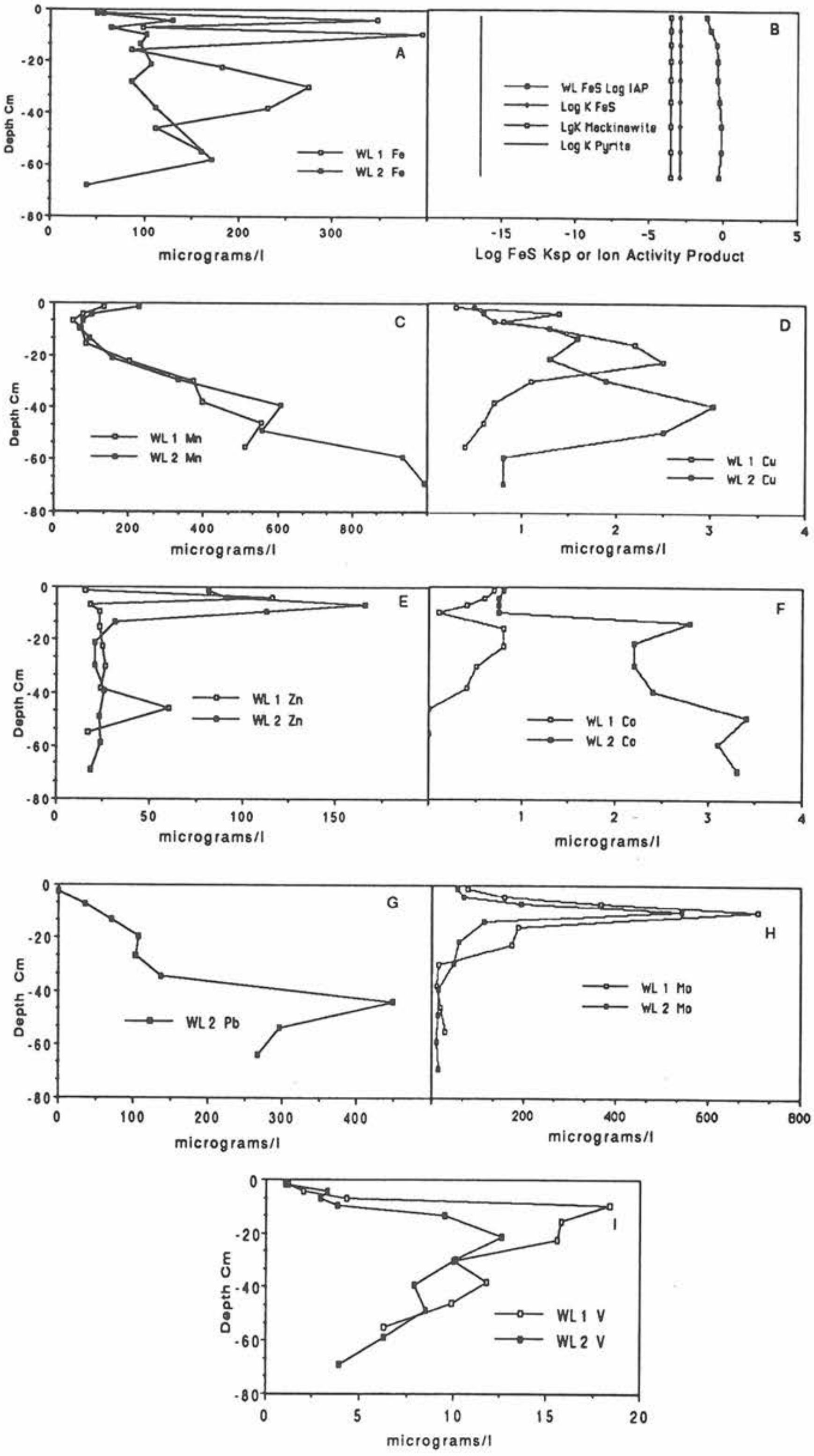


FIG. 4. Walker Lake pore-fluid trace metal concentrations and iron sulfide activity product profiles: a) Fe; b) FeS ion activity product and saturation indices for mackinawite, amorphous FeS and pyrite; c) Mn; d) Cu; e) Zn; f) Co; g) Pb; h) Mo; i) V.

Table 3. Walker Lake sediments. Total extractable and total sedimentary metals

Iron concentrations: milligrams/gram
All other metals: micrograms/gram
Core location: WL2

Depth (cm)	Fe	Mn	Cu	Zn	Pb	Co	Cd	Mo	V
Total extractable metals									
2.5	10.6	543	28.0	38.9	11.5	4.6	0.1	25.3	62.2
7.5	9.7	533	26.5	35.8	10.0	6.3	0.1	27.4	61.6
13.5	9.9	557	27.3	33.2	11.4	7.4	0.12	24.1	85.3
21.0	11.3	640	35.2	34.0	10.0	8.3	0.16	5.3	70.0
29.5	8.0	535	26.7	31.7	9.2	6.0	0.12	7.9	49.5
39.0	10.5	587	28.6	39.3	10.2	9.0	0.15	2.7	35.7
49.0	14.7	538	26.4	42.8	7.9	4.8	0.07	1.8	29.2
59.0	16.1	660	34.3	52.4	8.7	6.1	0.1	1.7	38.4
69.0	13.2	641	32.8	43.5	10.1	7.4	0.15	3.0	36.2
Total sedimentary metals									
2.5	38.0	670	44.0	81.0	16.0	16.0	<1	44.0	110
19.5	33.0	670	43.0	68.0	16.0	13.0	<1	63.0	140
34.5	40.0	630	49.0	84.0	12.0	15.0	<1	17.0	98
46.5	43.0	740	49.0	92.0	20.0	17.0	<1	9.0	94
62.0	42.0	820	51.0	87.0	14.0	16.0	<1	13.0	88

humic acids account for 6.4, 1.2, and 7.8% of the TOC, respectively.

Walker Lake sequential and humic acid extractions

Site WL2 was chosen for sequential extraction experiments. The results for Fe and Mn are shown in Fig. 7. Iron was unreactive to distilled/de-ionized water and neutral exchanger but was extracted by the acid cation exchanger and the reducing and oxidizing solutions. The most reactive zones for the reducing solution are at 30 cm and the bottom two core sections. The amount of sequential extractable Fe is greatest near the bottom of the core where 10 to 11% of the aqua regia extractable is recovered. This region of the core shows the greatest amount of reactivity. Above 30 cm the oxidizing solution tends to extract the most Fe whereas below 30 cm the reducing solution extracts the most. The peroxide extractable Fe in the upper part of the core is probably derived from algal debris and sulfides, whereas the reducing solution attacks dissolving oxides in the lower part of the core. Some of the peroxide extractable Fe is from FeS as the pore fluids are supersaturated with respect to this mineral throughout the core. The concentration of humic-acid bound Fe is greatest in the bottom two core

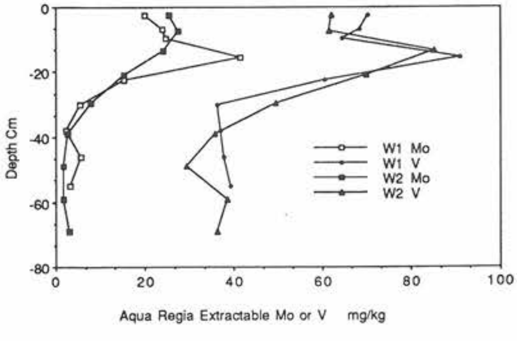


FIG. 5. Aqua regia extractable Mo and V from Walker Lake sediments.

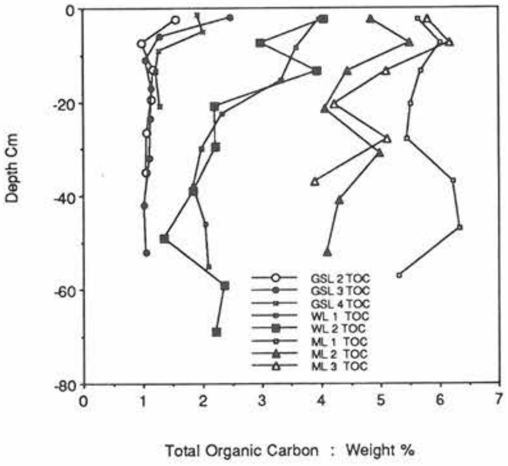


FIG. 6. Sedimentary total organic carbon at Walker, Mono and Great Salt Lakes.

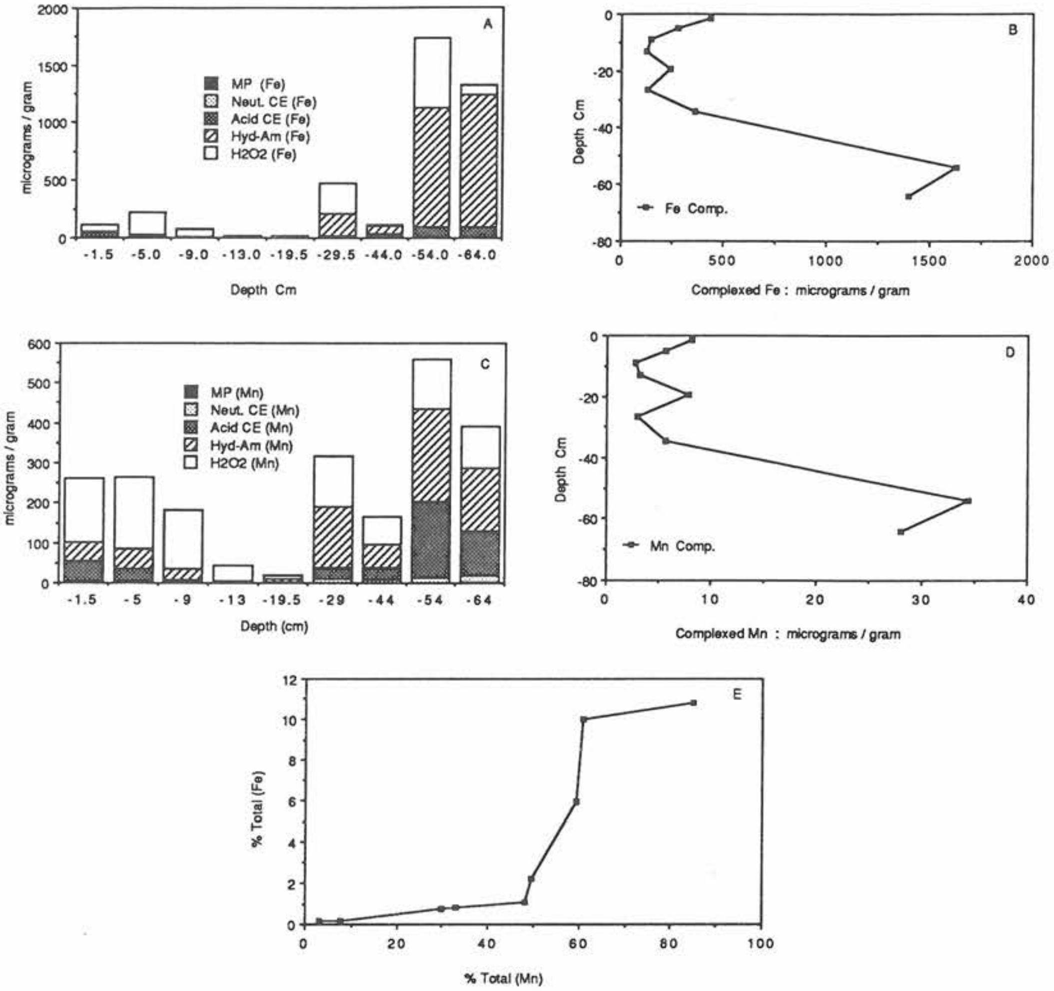


FIG. 7. Sequential and humic acid extraction results for Fe and Mn from Walker Lake sediments; The patterns represent results for each extraction (MP: Millipore water; Neut. CE: neutral cation exchanger; Acid CE: acidic cation exchanger; Hyd-Am: hydroxylamine hydrochloride or the reducing solution; H_2O_2: hydrogen peroxide or the oxidizing solution): a) Fe sequential extraction; The largest stack represents 4.2% of total sedimentary Fe; b) Fe humic acid extraction; The greatest amount of complexed Fe is 4% of the total; c) Mn sequential extraction; The largest stack represents 73% of total sedimentary Mn; d) Mn humic acid extraction; The greatest amount of complexed Mn is 4.5% of the total; e) comparison of Fe and Mn reactivity to sequential extraction solutions.

sections. In these horizons about 10% of the aqua regia extractable Fe is present as humic acid complexes.

Manganese was also unreactive to the distilled/deionized water and neutral cation exchanger extractions. Approximately 30% of the aqua regia extractable Mn was recovered with hydrogen peroxide on samples from the sediment-water interface. Sequential extractable Mn decreased to the 20 cm horizon and then tended to increase to the bottom of the core. The largest amount of Mn, 80% of the aqua regia extractable, was recovered at 55 cm. Similar to the situation with Fe, hydrogen peroxide extracted the most in the upper part of the core; hydroxylamine hydrochloride extracted more in the lower part. This may be accounted for by oxidation of algal debris in the upper part of the core and attack of dissolving oxides below. The humic acid bound Mn profile is very similar in shape to that for Fe. However, less than 5% of the aqua regia extractable Mn is complexed to humic acid. The acid cation exchanger also extracts a significant amount of Mn. This may be from dissolution of carbonates or, alternatively, from the exchange of Mn from active surface sites by proton exchange.

A comparison of the percent of Fe and Mn recovered by sequential extraction solutions is shown in Fig. 7e. The figure shows that Fe reactivity is low until the point where about 50% of the Mn is recovered. The data is consistent with the redox chemistry of these elements. Manganese oxides decompose at a higher pe than Fe. Therefore, its reactivity will precede that of Fe down a sedimentary redox gradient. The pore-fluid profiles for Mn show increasing concentrations with depth, and reactivity to the reducing solution increases below the 20 cm horizon indicating that the dissolving phase is an oxide. The Mn oxides are dissolving prior to the Fe oxides whose reductive dissolution is initiated near the 50 cm horizon. Dissolved Mn^{2+} is re-adsorbed to Fe oxides at and above this horizon. This is indicated by the humic acid results which show the greatest amount of Mn and Fe complexation in the same horizons. Apparently, Fe oxides outcompete humic acid for adsorption of reduced Mn. Manganese is released from the surfaces of dissolving Fe oxide and some is adsorbed onto humic acid. The reduced Fe is either complexed to humic acid or precipitates as FeS. Pyrite does not precipitate because the pore fluids must first be undersaturated with respect to FeS before this can occur according to MORSE *et al.*, 1987.

The sequential and humic acid extraction profiles for Cu, Zn, Pb, Co, and Cd are shown in Fig. 8. Copper is mobilized by the oxidizing solution. The greatest amount recovered was close to 10% of the aqua regia extractable Cu at the 5 cm horizon. The sequential extractable Cu decreases to the 20 cm horizon and then increases to the bottom of the core. A greater amount of Cu is complexed to humic acid. Close to 20% of the aqua regia extractable Cu is complexed near the 20 cm horizon and at the bottom of the core. The solid phase transformations of Cu are difficult to interpret. The only reactivity is to the oxidizing solution and the humic acid extraction. This is typical for Cu extractions and has been observed in a number of other sedimentary samples, as discussed by MARTIN *et al.*, 1987. Some Cu apparently is associated with oxide phases. Pore-fluid Cu concentrations are lowest at the sediment-water interface near the Fe oxide gel. Dissolved Cu concentrations are also generally low throughout the core. Copper extractability and humic acid complexation increase below 20 cm which might be attributed to the liberation of Cu from dissolving oxides.

The sequential extraction chemistry of Zn is dominated by two horizons. The first is near the 5 cm horizon where the greatest amount, about 12% of the aqua regia extractable, is recovered. The pore-fluid Zn concentrations are also highest at this depth. All solutions extract some Zn at the 5 cm horizon. The acid cation exchanger extracts the most. Reactivity to hydroxylamine hydrochloride is greatest for the bottom two core sections. Hydrogen peroxide extracts the most Zn at the 5 and 55 cm horizons. The humic acid bound Zn profile is very similar to those for Fe and Mn. About 11 to 12% of the aqua regia extractable Zn is complexed to humic acid near the bottom of the core. The extractability of Zn with the oxidizing solution in the upper part of the core suggests that Zn is released from decomposing algal debris or sulfides. It is known that phytoplankton accumulate Zn (VINOGRADOVA and KOVALSKIY, 1962; BOSTROME *et al.*, 1974). Iron oxides also adsorb Zn out of solution (BENJAMIN and LECKIE, 1981). These may be the two major sources of sedimentary Zn. Reactivity to the acid cation exchanger may be due to desorption from the active sites of metal oxides or clay minerals. There is evidence for adsorption of Zn onto Fe oxides. This is indicated by the relatively lower pore-fluid concentrations at the sediment-water interface, the release of Zn by the reducing solution in the lower two core sections, and the greatest complexation of Zn by humic acid in the lower two core sections. The extraction results suggest a number of possible sedimentary residences of Zn which include carbonates, oxides, humic acid, and sulfides.

Lead is extractable with the reducing and oxidizing solutions. The oxidizer always extracts the most. The greatest reactivity to the reducing solution is at and below 55 cm, which is similar to Fe. The horizon of greatest reactivity is at 55 cm where close to 30% of the aqua regia extractable is recovered. The shape of the humic acid complexed Pb profile is very similar to that for Fe, Mn, and Zn. This suggests that some Pb is transferred to humic acid following the dissolution of Fe oxide. The greatest percentage of complexed Pb, about 10% of the aqua regia extractable, is at the bottom two core horizons. The sequential and humic acid extractions suggest that Pb is affected by the presence of Fe oxides throughout the core. Oxides have the dominant effect on Pb geochemistry in this sedimentary interval. Although the experiments suggest that some Pb is transferred to humic acid during oxide dissolution, it is not possible to infer the nature of other authigenic Pb phases. As the oxidizing solution extracts the greatest amount of Pb it is possible that precipitation of Pb sulfide or co-precipitation with other metal sulfides occurs.

The sequential extraction of Co is dominated by reactivity to the oxidizing solution. The reactivity is high in the upper 5 cm, decreases at the 20 cm horizon, and then tends to increase at the bottom of the core. The acid cation exchanger extracts some Co in the upper 5 cm and the reducing solution extracts some in the lower two core sections. Between 10 to 15% of the aqua regia extractable Co is complexed to humic acid throughout the core except for the 55 cm horizon where close to 50% is complexed. The geochemistry of Co is probably controlled by Fe and Mn oxides throughout the length of the core as suggested by the extraction profiles. This is indicated by the greatest reactivity to the reducing solution and the highest amount of humic acid complexation occurring near the bottom of the core. The reactivity to peroxide in the upper 10 cm is probably due to oxidation of algal debris or sulfides. Solubility calculations suggest that a Co sulfide should form in these sediments.

Cadmium is extractable only by the oxidizing solution. In most core sections the oxidizing solution quantitatively extracts the aqua regia extractable Cd. Cadmium is not complexed to humic acid. The Cd extracted by peroxide is either bound to non-humic organic matter or to sulfides. There is no evidence for Cd adsorption onto oxides within these sediments. Results from laboratory experiments (Benjamin and Leckie, 1981) show that Cd is less reactive to adsorption onto oxides as compared to the other cationic metals in this study. Cadmium is probably outcompeted for adsorption sites on these oxides and precipitates as a discrete sulfide.

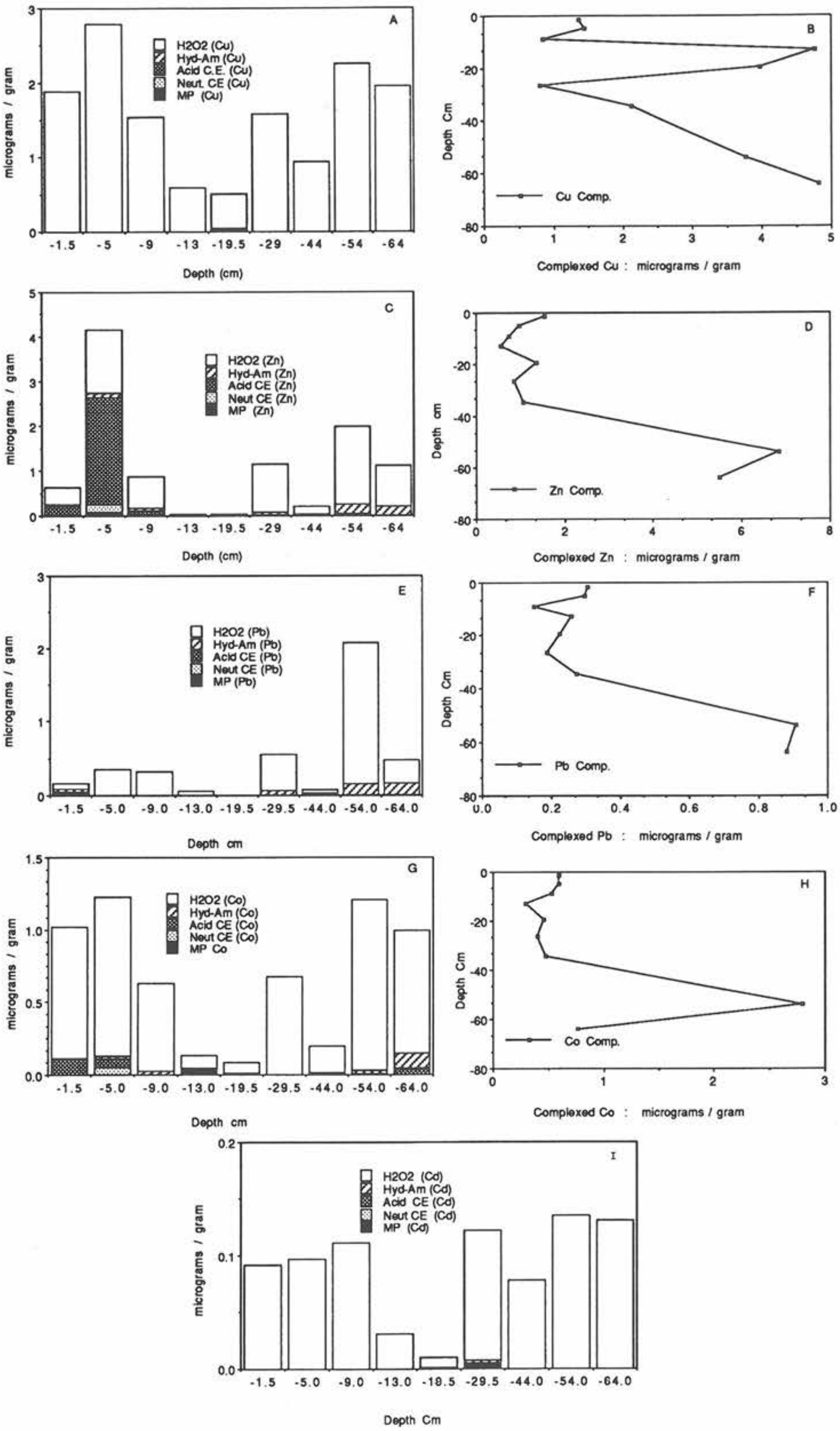
The extraction profiles for Mo and V are shown in Fig. 9. Molybdenum is quantitatively recovered by sequential extraction reagents from Walker Lake sediments, except for the sediment-water interface. The highest concentrations are recovered at the 10 cm horizon due to diagenetic redistribution. Less than 20% of the aqua regia extractable Mo is recovered at the sediment-water interface. Below, there is an easily extractable form which is released by distilled/de-ionized water and the neutral cation exchanger. The acidic cation exchanger and the reducing solution extract progressively smaller amounts. Hydrogen peroxide extracts the more refractory Mo in amounts comparable to the first two extractants. Molybdenum is also effectively extracted by sodium hydroxide. However, there is no association of Mo with humic acid. Humic acid can be quantitatively separated from Mo by gel permeation chromatography. This is consistent with the results of Disnar (1981) who showed that acidic conditions, below pH 3, are required for the adsorption of Mo onto sedimentary organic matter.

The pore-fluid and selective extraction results show that Mo solubility is quite low at the sediment-water interface. Only sodium hydroxide, at pH 13, is capable of extracting Mo from this horizon. In oxidizing streams Mo has been found in association with Fe oxides (Kaback and Runnells, 1980) whereas for reducing sediments, such as the Black Sea, Mo precipitates as a discrete sulfide or in association with Fe monosulfides (Korolov, 1958; Volkov and Fomina, 1974; Bertine, 1972). Molybdenum may be adsorbed to the Fe oxide gel near the sediment-water interface. However, there is no evidence for adsorption of Mo onto oxides below this region.

The most likely mechanism for the sedimentary Mo re-distribution involves redox chemistry. Within the enriched zone Mo can be transported as the oxidized molybdate ion. Sufficient sulfide is present below to immobilize the metal, possibly by co-precipitation with Fe monosulfide. The Mo sulfide which forms is stable only in the presence of dissolved sulfide. It can be extracted by the anoxic sodium hydroxide extraction, and is partially extractable with other reagents. The peroxide extractable Mo in the deeper part of the core is probably associated with Fe monosulfides which can be dissolved with this reagent. The highest solubility of Mo is within the horizon below the Fe oxide gel and above the region of Mo sulfide precipitation.

Vanadium is also affected by diagenetic re-distribution at Walker Lake. The mechanism has some similarities to that for Mo but the redox speciation of V results in different solid phase associations. Only the reducing and oxidizing solutions extract this metal. The percent of V recovered by the sequential extraction relative to the aqua regia extractable is shown in Fig. 9c. The greatest extractability occurs just above the sedimentary horizon of highest total V. Extractability tends to decrease below this horizon. Unlike Mo, V does have an association with organic matter. The bottom two core horizons have the greatest amount of humic acid complexed V, about 10% of the aqua regia extractable. The shape of the humic acid bound V profile is similar to those already shown for Fe, Mn, Zn, and Pb.

In alkaline, oxidizing environments dissolved V is present as some type of an oxyanion such as HVO_4^{2-} (Hem, 1977). Under reducing conditions and at the pH of Walker Lake pore fluids, V should be present as the oxycation, $V(OH)_2^+$ (Hem, 1977). The transition occurs somewhere below 10 cm. The oxycation readily adsorbs onto oxides at the pH of these pore fluids and is also complexed by humic acid or other organic compounds. The association of V with Fe oxides below 10 cm is supported by the similarity in the shape of the humic acid complexed metal profiles for these two metals. The highest concentrations of humic acid bound Fe and V occur near the bottom of the core due to reductive


A
H2O2 (Cu)
Hyd-Am (Cu)
Acid C.E. (Cu)
Neut. CE (Cu)
MP (Cu)
micrograms / gram
0
1
2
3
-1.5
-5
-9
-13
-19.5
-29
-44
-54
-64
Depth (cm)
B
Cu Comp.
Depth Cm
0
-20
-40
-60
-80
1
2
3
4
5
Complexed Cu : micrograms / gram
C
H2O2 (Zn)
Hyd-Am (Zn)
Acid CE (Zn)
Neut CE (Zn)
MP (Zn)
micrograms / gram
4
Depth (cm)
D
Zn Comp.
Depth cm
6
8
Complexed Zn : micrograms / gram
E
H2O2 (Pb)
Hyd-Am (Pb)
Acid CE (Pb)
Neut CE (Pb)
MP (Pb)
-5.0
-9.0
-13.0
-29.5
-44.0
-54.0
-64.0
Depth cm
F
Pb Comp.
0.0
0.2
0.4
0.6
0.8
1.0
Complexed Pb : micrograms / gram
G
H2O2 (Co)
Hyd-Am (Co)
Acid CE (Co)
Neut CE (Co)
MP Co
0.5
1.5
H
Co Comp.
Complexed Co : micrograms / gram
I
H2O2 (Cd)
Hyd-Am (Cd)
Acid CE (Cd)
Neut CE (Cd)
MP (Cd)
0.1
Depth Cm

dissolution of Fe oxides and subsequent adsorption of the two reduced metals. The decrease in V reactivity to sequential extraction solutions below 10 cm of sediment is due to reduction and adsorption onto Fe oxide or organic matter. Like Mo, V has low pore-fluid concentration and low extractability near the sediment-water interface. This may also be due to adsorption on the freshly precipitated Fe oxide gel. The sedimentary re-distribution is a result of the diffuse redox gradient in Walker Lake sediments. Vanadium has highest solubility in the pore fluids close to the 10 cm horizon. The high solubility implies that V is present as an oxyanion in this region. Below this horizon V is immobilized by reduction and is adsorbed onto Fe oxides or is complexed by organic matter. Vanadium is mobilized at and below the 55 cm horizon due to reductive dissolution of Fe oxides.

Walker Lake summary

Walker Lake is a monomictic alkaline closed basin lake at an early stage of brine evolution. The sediment-water interface is oxygenated throughout most of the year except during late summer thermal stratification. The combination of oxygenated waters and high pH results in very low trace metal concentrations throughout the water column due to the scavenging of fine particulate oxides and organic matter. Changes in water chemistry occur across the sediment-water interface, which affect trace metals. This includes a drop in pH, due to carbon dioxide release from decomposing organic matter, and the production of hydrogen sulfide. The two sampling sites differ in that WL2 is at the hydrographic low of the basin coincident with buried brines and salts from past desiccation events. These brines are now diffusing to the sediment-water interface. Upward diffusion of dissolved carbonate species results in a higher buffering capacity of the pore-fluid brine relative to site WL1. Sulfate reduction goes to completion at site WL1, near 55 cm of sediment, but adequate sulfate is available at the same horizon of WL2 for further sulfide production. The abundant sulfate at site WL2 is in part from brine diffusion.

The trace metal chemistry in Walker Lake sediments is influenced by the presence of Fe and Mn oxides and hydrogen sulfide, which are present throughout the core. The reductive dissolution of Mn oxides begins before Fe oxides. Some adsorption of Mn^{2+} onto Fe oxide occurs after the dissolution of Mn oxide. Evidence for the presence of metal oxides and their influence on trace metals was provided by the following data: the reactivity of Fe to the reducing solution was greatest at the bottom of the core; a concentration increase in humic acid bound Fe coincides with the same core horizons as increases in the concentration of humic acid bound trace metals (Mn, Zn, Pb, Co, Cu, V). The results suggest the transfer of Fe from dissolving oxides to humic acid. Trace metals, initially bound to Fe or Mn oxides, are adsorbed on the humic material as they are released to the pore fluids by reductive dissolution. The humic acids are therefore secondary sinks of metals, following the reductive dissolution of metal oxides. Other secondary sinks include sulfides. The Walker Lake pore fluids are supersaturated with respect to Fe monosulfides which probably precipitate throughout this sedimentary interval. The degree of supersaturation is about two log units which inhibits the formation of pyrite. Solubility calculations suggest that the pore fluids may be supersaturated with respect to the sulfides of Cu^{+}, Zn^{2+}, Pb^{2+}, and Co^{2+}. However, there is insufficient information on the pore-fluid speciation of these metals to determine if they are in equilibrium with pure sulfide phases. Co-precipitation with Fe monosulfides is possible but the extraction experiments show no conclusive proof of this.

In addition to Fe monosulfides there is precipitation of diagenetically mobilized Fe oxide at the sediment-water interface. The source of this Fe is most likely algal debris as the Fe oxides are not labile to reduction in this region. This is supported by the sequential extraction data which showed that hydrogen peroxide released the most Fe near the sediment-water interface. The Fe released from decaying algal debris either precipitates as a sulfide or migrates to the sediment-water interface where oxidation occurs. The presence of this oxide layer near the sediment-water interface has important impacts on dissolved trace metals. It is a recently precipitated hydrous Fe oxide which can adsorb trace metals.

FIG. 8. Sequential and humic acid extraction results for Cu, Zn, Pb, Co, and Cd from Walker Lake sediments: a) Cu sequential extraction; The largest stack represents 6.4% of total sedimentary Cu; b) Cu humic acid extraction; The greatest amount of complexed Cu is 11% of the total; c) Zn sequential extraction; The largest stack represents 5.1% of total sedimentary Zn; d) Zn humic acid extraction; The greatest amount of complexed Zn is 8.4% of the total; e) Pb sequential extraction; The largest stack represents 14.8% of total sedimentary Pb; f) Pb humic acid extraction; The greatest amount of complexed Pb is 6.5% of the total; g) Co sequential extraction; The largest stack represents 7.5% of total sedimentary Co; h) Co humic acid extraction; The greatest amount of complexed Co is 17.4% of the total; i) Cd sequential extraction; Most stacks represent 100% of aqua regia extractable Cd.

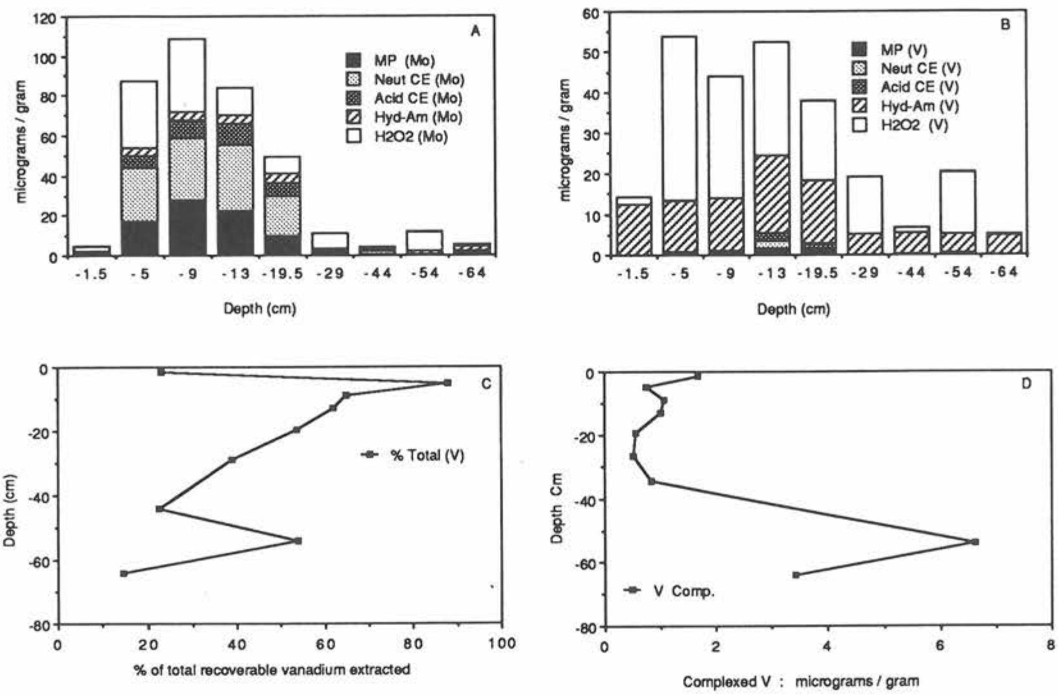


FIG. 9. Sequential and humic acid extraction results for Mo and V from Walker Lake sediments: a) Mo sequential extraction; Most stacks represents 100% of total sedimentary Mo; b) V sequential extraction; Most stacks represent 50% of total sedimentary V; c) % of total extractable V recovered by sequential extraction; d) V humic acid extraction; The greatest amount of complexed V is 7% of the total.

Furthermore, it is located near the sediment-water interface at a pH near 9 which is ideal for the adsorption of metal cations. Consistent with this, the pore-fluid trace metal concentrations tend to be lowest near this gel, relative to other core horizons.

The geochemistry of Cd is distinct from that of Fe, Mn, Cu, Zn, Pb, and Co. The evidence for this is with the sequential extraction data, in particular, the percent Cd extracted relative to the aqua regia extractable. For most core horizons Cd is quantitatively extractable with hydrogen peroxide. Cadmium is probably precipitating as a discrete sulfide. Cadmium is less reactive to adsorption onto Fe and Mn oxides relative to the other trace metals (BENJAMIN and LECKIE, 1981). In the sulfidic environment Cd is most likely extracted from oxide surfaces and precipitated as a sulfide. There is no evidence of humic acid complexation of Cd.

The oxyanion forming elements, Mo and V, have a sedimentary geochemistry based on redox conditions which results in diagenetic re-distribution. The redox chemistry of Walker Lake sediments is ideal for this mobilization as a diffuse gradient of pe, from oxygen saturation to Mn oxide dissolution to Fe oxide dissolution, occurs over an interval of 1 meter of sediment. Both Mo and V migrate to the upper region of sediment in the oxyanion form. The oxyanions are resistant to adsorption and hence migrate to sedimentary environments of higher pe. Molybdenum is immobilized by sulfide precipitation. Vanadium is immobilized by reduction to an oxycation adsorbed onto oxide surfaces or complexed by organic matter.

Sequential extraction procedures recover various amounts of trace elements from Walker Lake sediments. The highest recoveries (100% relative to the aqua regia extractable) are for Mo and Cd. The lowest recoveries (less than 1% to 24%) are for Fe, Zn, Cu, and Pb. This is probably caused by the presence of Fe oxides throughout the core. The recovery of cobalt is higher in most horizons relative to Fe, Zn, Cu, and Pb, but is always lower than Mn. Manganese recovery is much higher, up to 85% of the aqua regia extractable, which is probably related to the dissolution of labile oxides. Humic acids are a significant sink for Fe, Zn, Co, V, and Pb in the lower part of the core and a significant sink for Cu throughout. Up to 20% of the aqua regia extractable Cu is present as humic acid complexes. Humic acids account for 10 to 15% of the aqua regia extractable Fe, Zn, Pb, and V. Cobalt complexation is highest at the 55 cm horizon where it accounts for 47% of the aqua regia extractable. Humic acids are an insignificant to minor sink for Mn. The greatest amount of complexation is 5% of the aqua regia extractable Mn at the bottom of the core.

Deeper cores, from both sites, are required to determine the diagenesis of metals associated with unstable solids, such as Fe monosulfides and humic acids. A comparison of sulfide mineralogy and organic matter, as trace metal sinks, could be made in the high and low sulfate environments.

Mono Lake brine chemistry

Mono Lake contains a Na-CO_3-Cl-SO_4 water with a pH near 9.65. A chemocline was present at 15 to 18 m of depth during the summers of 1985 and 1986. The deepest part of the lake sampled was 32 m. The ionic strength of the mixolimnion was 1.6 and that of the bottom brines was 1.9. The concentrations of the major elements in the water column are listed in Table 4 and the water column and pore-fluid profiles of sodium, alkalinity, sulfate, sulfide, and DOC are shown in Fig. 10. The lake is in an advanced state of brine evolution. The high alkalinity is an effective pH buffer and the high pH provides a favorable environment for trace metal adsorption onto Fe and Mn oxides.

Sulfate behaves non-conservatively in the water column. The concentration increases across the chemocline but appears to drop near the bottom of the lake (Fig. 10). The drop can be attributed to the initiation of sulfide production. Sulfide concentration in the bottom brine was 182.7 micromoles/l at 25 m of depth and 423.2 micromoles/l at 32 m of depth during this sampling. At a pH of 9.65 almost all of this sulfide is in the HS^- form. At a pH above 9 the bottom brines are also an ideal environment for the formation of polysulfide species which are effective ligands for trace metals (BOULEGUE and MICHARD, 1978). The calculated pe of the bottom brine, from the SO_4^{2-}/HS^- redox couple, is −6.25 which is sufficiently negative to result in the reductive dissolution of Mn and Fe oxides. The lake waters contain high levels of DOC. The concentrations are listed in Table 4. The high pH and evaporative concentration are probably most responsible for the high DOC levels. The high pH waters are probably effective in hydrolyzing algal debris and thus contributing to the DOC. Algal productivity is high and has been measured at 340 to 550 g C/m^2/year (JELLISON and MELACK, 1988). The lake water DOC may affect the chemistry of trace metals but this was not investigated in this study.

The pore-fluid concentrations of major elements decrease with depth as illustrated by the Na^+ profile (Fig. 10b). Alkalinity and chloride have the same trend. The lake and pore-fluid brines are out of equilibrium. The rapid evaporative drawdown of the lake has resulted in more concentrated brines in the water column relative to the pore fluids. Despite the drop in alkalinity the pore fluids are well buffered against changes in pH. The pH drops only slightly in the sediments from 9.65 to 9.24. Pore-fluid sulfate decreases in concentration more markedly than the other major solutes because of reduction. The sulfide profiles are shown in Fig. 10f. The sulfate:sulfide ratio is shown in Fig. 10g. A polynomial equation derived from this data predicts that sulfate reduction should go to completion at a depth near one m of sediment. The calculated pe of the pore fluids, based on the SO_4^{2-}/HS^- ratio, is −6.37 at the sediment-water interface and decreases to −6.16 at 65 cm.

Table 4. Mono Lake water column. Concentration of major elements and dissolved organic carbon

	Ion concentration: milligrams/liter Dissolved organic carbon concentration: milligrams/liter Alkalinity: milliequivalents/liter							
Depth (m)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	ALK	DOC
1	30660	1610	38.9	10.3	9430	5040	630	N.A.*
5	30660	1640	38.9	6.7	9570	5300	634	78.9
10	30780	1640	39.3	5.5	9550	5170	625	79.9
15	30420	1630	38.8	6.1	9600	5250	632	88.4
20	30900	1650	39.6	6.1	9830	5240	645	79.1
25	32720	1760	41.3	5.7	10270	5640	691	87.6
30	34410	1840	43.2	5.2	10910	6010	709	86.4
34	35140	1890	43.7	5.8	11210	5880	719	89.4

* N.A. Not analyzed.

The pore fluids have high concentrations of DOC. The concentrations at sites ML1 and ML2 are similar, but site ML3 is lower. The DOC of the pore fluids is composed of hydrophilic acids which are capable of complexing metals (DOMAGALSKI, 1988). These acids have a structure which is similar to Mono Lake humic acids as determined by ^{13}C nuclear magnetic resonance spectroscopy (DOMAGALSKI, 1988). This was the only lake for which a sufficient amount of pore-fluid DOC was recovered for this type of analysis. Although the DOC of Walker Lake pore fluids was not investigated by NMR spectroscopy it is likely to be structurally similar to the DOC of Mono Lake. Both Walker and Mono Lakes have similar humic acid NMR spectra and the DOC in both lakes is derived from the decomposition of algal material in an anoxic environment (DOMAGALSKI, 1988). The molecular weight of the Mono Lake pore-fluid DOC is at least greater than 500 atomic mass units. Most of the

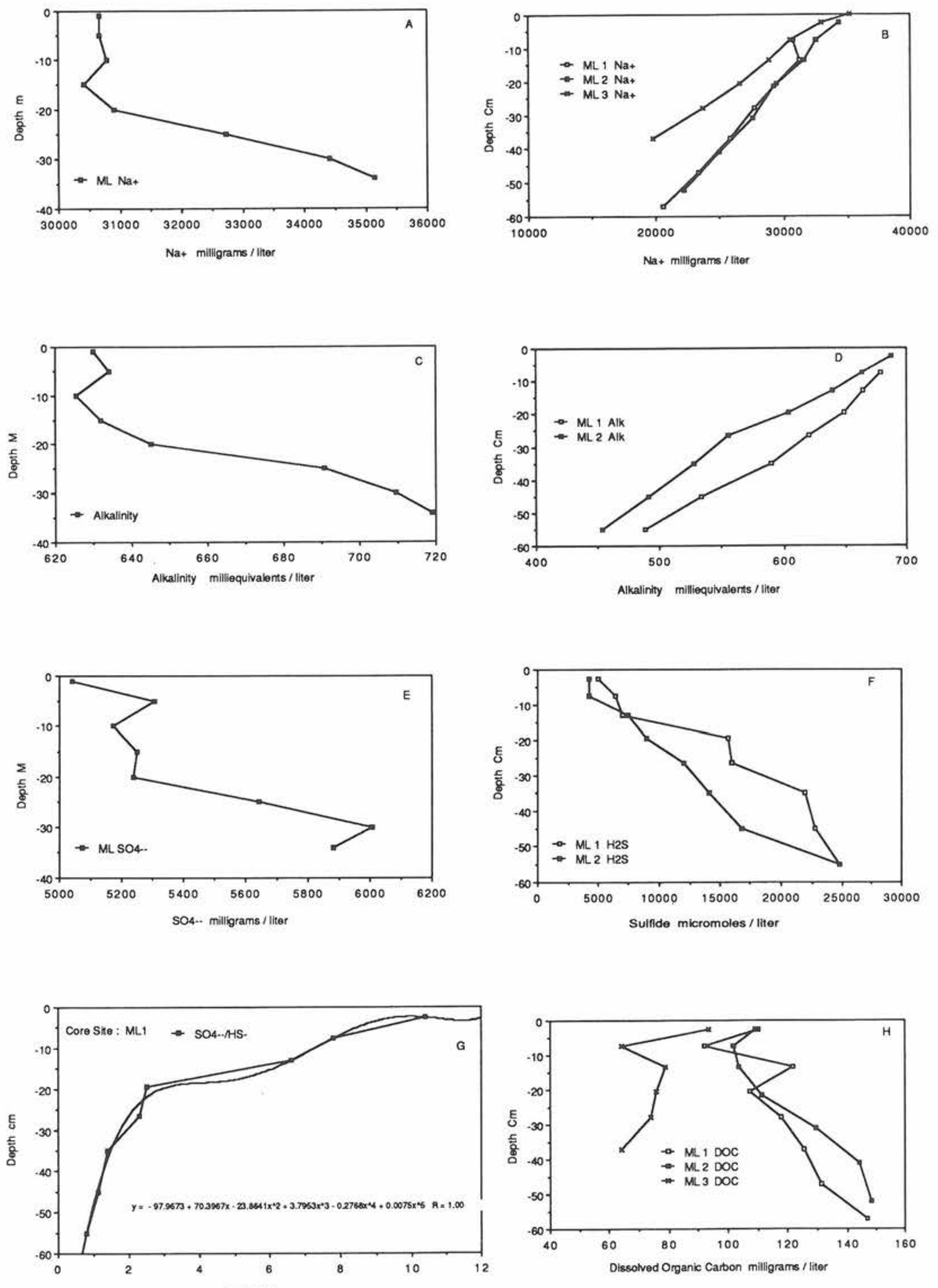


FIG. 10. Mono Lake water column and pore-fluid major element geochemistry: a) water column Na^+; b) pore-fluid Na^+; c) water column alkalinity; d) pore-fluid alkalinity; e) water column sulfate; f) pore-fluid sulfide; g) pore-fluid SO_4^{--}/HS^- ratio; h) pore-fluid dissolved organic carbon.

Table 5. Mono Lake water column. Trace metals

Depth (m)	Metal concentration: micrograms/liter								
	Fe	Mn	Cu	Zn	Co	Mo	V	Cd	Pb
5	210	38.0	7.1	17.3	0.5	49.2	16.3	0.5	N.D.*
10	695	52.5	9.5	16.8	0.3	82.0	17.9	N.A.**	N.D.
15	833	65.9	8.9	15.5	0.9	77.0	N.A.	0.5	N.D.
20	526	40.6	6.9	16.8	0.7	84.0	17.5	N.A.	N.D.
25	258	60.5	5.0	18.0	N.D.	80.1	20.6	0.5	N.D.
30	153	63.0	6.4	16.8	N.D.	83.9	22.9	0.5	N.D.
34	129	71.6	7.6	16.8	N.D.	85.0	22.4	N.A.	N.D.

* N.D. Not detected.

** N.A. Not analyzed.

DOC was recovered by ultra-filtration using a membrane with this nominal cut-off.

The water column trace metal concentrations are given in Table 5. Iron concentration is highest near the chemocline and decreases with depth due to precipitation of FeS. The water column and pore-fluid trace metal profiles are shown in Fig. 11. Solubility calculations by WATEQ4F (BALL *et al.*, 1987) show that supersaturation with respect to all Fe sulfide polymorphs occurs in the bottom brines. The concentration of Fe continues to decrease across the sediment-water interface. The pore-fluid Fe profile is shown in Fig. 11c along with the concentration of Fe complexed to DOC. The uncomplexed Fe concentrations were used in WATEQ4F for solubility calculations. The results, graphically shown in Fig. 11d, show that supersaturation with respect to amorphous FeS, mackinawite, and pyrite occurs throughout the core. These calculations assume no solution complexing of Fe with bisulfide ions.

Manganese concentrations are also greatest in the anoxic bottom waters (Fig. 11b), but there is no evidence of precipitation. Manganese concentrations drop rapidly across the sediment-water interface. Only a small amount of the dissolved Mn is complexed to DOC (Fig. 11e). The bottom brines are undersaturated with respect to MnS. The log saturation index at 32 m of depth is −0.5. Across the sediment-water interface the saturation index increases to 0.6. Below 5 cm the ion activity products are close to the Ksp. The saturation indices were calculated using a pKsp of 0.4 (JACOBS and EMERSON, 1982). Authigenic Mn sulfides are rare in modern sediments and their presence has only been documented in the sediments of the Baltic (BOESEN and POSTMA, 1988).

Copper concentration is greatest near the chemocline, decreases below, and then increases in the bottom brine. Zinc concentrations are relatively uniform with depth. Lake water Cd concentrations are at detection limits. Lead concentration is below the detection limit of 0.5 micrograms/l. Cobalt concentrations are less than one microgram/l above the chemocline and undetectable below.

The pore-fluid Cu profile indicates mobilization in the upper 10 cm of sediment (Fig. 11f). Organic complexes of Cu increase in importance below this horizon. Zinc concentrations are also greatest just below the sediment-water interface. Lead is not detected in the pore fluids. Pore-fluid Cd concentrations are low but clearly detectable below 30 cm (Fig. 11i). This element was measured by differential pulse anodic stripping voltammetry and the sample peak was displaced from that of the pure standard by −40.0 mv throughout the pore fluids. This is taken as evidence that Cd is complexed to a polymolecular ligand in the pore fluids.

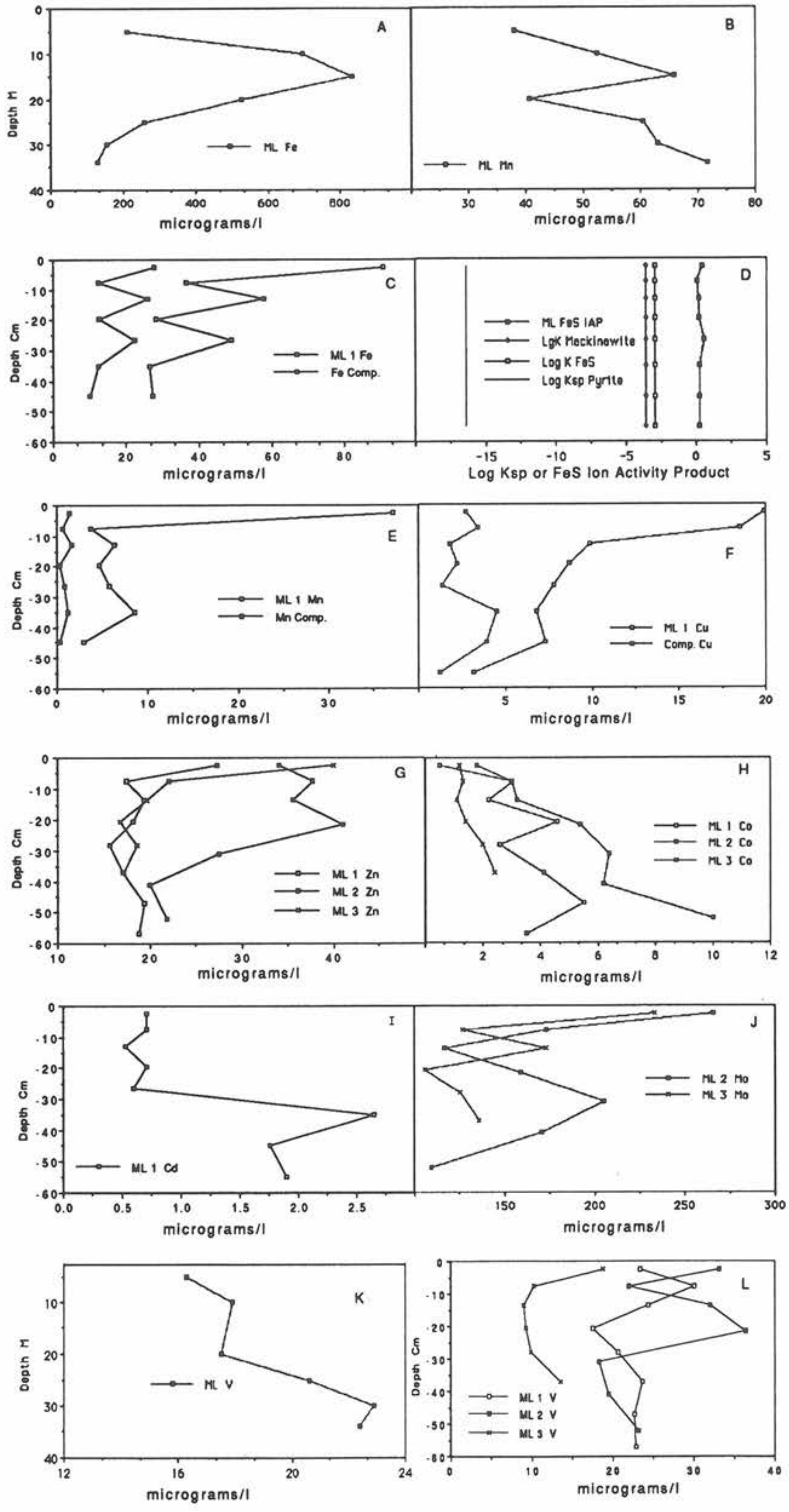
Cobalt pore-fluid profiles are similar at sites ML1 and ML2 but the concentrations are lower at site ML3 (Fig. 11h). Although Co was undetected in the sulfidic bottom brines of the lake, the Co concentrations tend to increase with the sulfide content of the pore fluids. It was not possible to determine if Co is complexed to DOC or other ligands. The pore-fluid profiles for the three sites suggest that Co and DOC concentrations are correlated. This can be seen by comparing the Co and DOC profiles in Figs. 10h and 11h. Solubility calculations for Cu^+, Zn^{2+}, Co^{2+}, and Cd^{2+} suggest extreme supersaturation with respect to metal sulfides. However the speciation of these metals in the pore fluids has not been defined. Possible ligands include polysulfide species and organic compounds.

Lake water V concentrations increase at the chemocline but there is little apparent mobilization in the pore fluids (Figs. 11k and 11l). The highest concentrations are at sites ML1 and ML2, which also have higher DOC relative to site ML3. This is similar to the profiles discussed for Co. In reducing waters V is present as an oxycation which can complex with hydrophilic acids. Molybdenum concentrations are lowest near the top of the water column with relatively higher and constant concentrations occurring at the bottom of the lake. A mobilization of Mo occurs in the upper 10 cm of sediment (Fig. 11j).

Mono Lake sedimentary chemistry

Mono Lake sediments are dominated by smectite clay minerals. Feldspars, derived from the Sierra Nevada Range, are also of importance. Aragonite is present in minor concentrations. The cores are black throughout, due to the presence of Fe monosulfides.

The concentration of aqua regia extractable metals and total metals are given in Table 6. Copper,


A
Depth M
ML Fe
micrograms/l
0
10
20
30
40
0
200
400
600
800
B
ML Mn
30
40
50
60
70
80
micrograms/l
C
Depth Cm
ML 1 Fe
Fe Comp.
0
-10
-20
-30
-40
-50
-60
0
20
40
60
80
micrograms/l
D
ML FeS IAP
LgK Mackinawite
Log K FeS
Log Ksp Pyrite
-15
-10
-5
0
5
Log Ksp or FeS Ion Activity Product
E
Depth Cm
ML 1 Mn
Mn Comp.
0
10
20
30
micrograms/l
F
ML 1 Cu
Comp. Cu
5
10
15
20
micrograms/l
G
Depth Cm
ML 1 Zn
ML 2 Zn
ML 3 Zn
10
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ML 1 Co
ML 2 Co
ML 3 Co
2
4
6
8
10
12
micrograms/l
I
Depth Cm
ML 1 Cd
0.0
0.5
1.0
1.5
2.0
2.5
micrograms/l
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ML 2 Mo
ML 3 Mo
150
200
250
300
micrograms/l
K
Depth M
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10
20
30
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12
16
20
24
micrograms/l
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ML 1 V
ML 2 V
ML 3 V
0
10
20
30
40
micrograms/l

Co, Zn, and V concentrations are below that of the "average black shale" of VINE and TOURTELOT (1970). Lead is close to that value and Mo is above. The total metal concentrations are higher than the corresponding aqua regia extractable. There is no apparent evidence for diagenetic re-distribution or anthropogenic enrichment of these metals.

The weight per cent of total organic carbon for the three coring sites is shown in Fig. 6. The highest concentrations are at site ML1. This may be due to its proximity to inflow streams which supply nutrients to the lake. Three horizons were analyzed for humic acid concentrations (0 to 16 cm, 23 to 30 cm, and 40 to 50 cm). Humic acids account for 8.4, 7.5, and 7.4% of the TOC in these horizons.

Mono Lake sequential and humic acid extractions

The extraction results for Fe and Mn are shown in Fig. 12. Iron can be extracted from Mono Lake sediments by the acidic cation exchanger, the reducing solution, and the oxidizing solution. In the upper 7 cm of core, the reducing solution releases the most Fe. Below, the oxidizing solution tends to release the most. There is very little Fe mobilized by the reducing solution between 13 to 20 cm. Below this horizon the amount mobilized by this reagent increases. This is probably due to crystalline oxides which only slowly dissolve in the anoxic environment. The most reactive zone for Fe is between 5 to 10 cm where close to 25% of the aqua regia extractable is recovered by sequential extraction solutions. The most unreactive zone is between 13 to 20 cm. Below this horizon the extractable Fe tends to be constant at values close to 10% of the aqua regia extractable. The amount of Fe complexed to humic acid is very low in Mono Lake sediments. In only two core sections does the amount exceed 1.0%. This suggests that the Fe released by the oxidizing solution is not organic but more likely is from a labile sulfide.

Manganese is extractable by the same three reagents. The maximum amount of reducible Mn is at the 9 cm horizon. The amounts extracted at and below the 13 cm horizon are always lower than those from above this horizon. The profiles for the acidic cation exchanger and reducing solution have a similar configuration. Throughout the core the oxidizing solution releases the most Mn. The greatest amount of Mn extracted by these reagents is at 9 cm where 43.4% of the aqua regia extractable was recovered. Below this horizon there is no significant change in reactivity and close to 25% of the aqua regia extractable was mobilized by selective sequential extractions.

Table 6. Mono Lake sediments. Total extractable and total sedimentary metals

Iron concentrations: milligrams/gram
All other metals: micrograms/gram
Core location: ML1

Depth (cm)	Fe	Mn	Cu	Zn	Pb	Co	Cd	Mo	V
				Total extractable metals					
2.5	12.3	318	21.6	53.3	15.0	5.7	0.21	14.3	32.1
7.5	13.2	326	21.3	58.5	10.5	4.6	0.26	17.8	37.0
13.5	9.9	293	17.8	48.6	15.0	4.5	0.33	14.4	33.8
20.5	9.5	338	15.7	44.6	12.1	4.4	0.27	10.7	38.5
28.0	13.2	392	22.9	58.8	13.4	5.0	0.35	18.6	39.9
37.0	10.9	331	18.1	53.3	9.8	5.3	0.27	18.3	41.2
47.0	9.4	318	15.4	44.2	9.0	4.4	0.29	27.8	34.1
57.0	12.0	362	22.8	52.3	7.6	7.4	0.30	35.3	31.4
				Total sedimentary metals					
28.0	26.0	530	31.0	86.0	18.0	11.0	<1	33.0	68.0
57.0	22.0	500	27.0	74.0	14.0	9.0	<1	61.0	66.0

The amount of Mn complexed to humic acid is extremely low in Mono Lake sediments. The highest amount is only 0.7% of the aqua regia extractable between 15 to 20 cm of depth. As with Fe, this suggests that the metal extracted with the oxidizing solution is not organically complexed but more likely is a sulfide.

The water chemistry data shows that the reductive dissolution of Fe and Mn oxides is initiated near the chemocline and the reactivity to hydroxylamine hydrochloride suggests that the greatest amount of reducible metal is present in the upper ten cm of sediment. Iron sulfide precipitation occurs in the water column and continues in the sediments as the oxides are reduced. Solubility calculations with WATEQ4F (BALL *et al.*, 1987) show that the bottom brines are supersaturated with respect to Fe monosulfides. This supersaturation continues through the sediments. Pyrite does not form in these sediments despite high supersaturation. Pyrite was not detected in X-ray diffraction patterns from

FIG. 11. Mono Lake water column and pore-fluid trace metal concentrations: a) water column Fe; b) water column Mn; c) pore-fluid Fe, total and complexed by DOC; d) pore-fluid FeS ion activity products and saturation indices for amorphous FeS, mackinawite, and pyrite; e) pore-fluid Mn, total and complexed by DOC; f) pore-fluid Cu; g) pore-fluid Zn; h) pore-fluid Co; i) pore-fluid Cd; j) pore-fluid Mo; k) water column V; l) pore-fluid V.

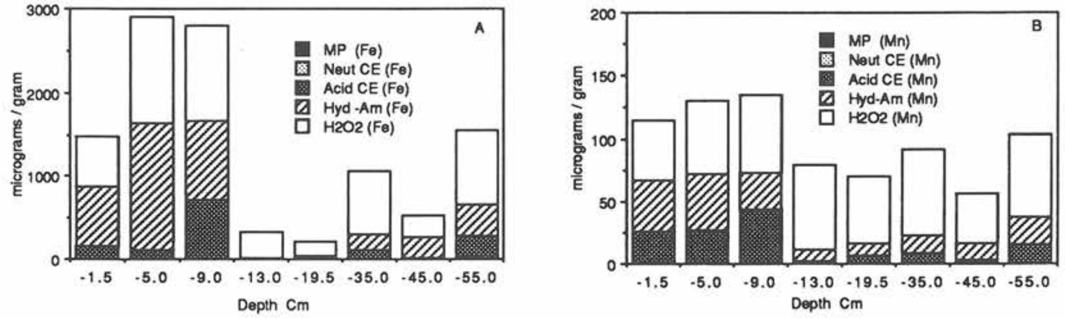


FIG. 12. Sequential extraction results for Fe and Mn from Mono Lake sediments: a) Fe; The largest stack represents 12% of total sedimentary Fe; b) Mn; The largest stack represents 26% of total sedimentary Mn.

mineral grains separated from the bulk sediment by bromoform extraction. Apparently the initial precipitation of FeS is kinetically favored. All other factors for pyrite formation are ideal in these sediments. Elemental sulfur, required for pyrite precipitation, should be abundant in the sediments because of reduction reactions involving HS^- and metal oxides. The supersaturation with respect to metastable Fe monosulfides prevents the formation of pyrite. Direct precipitation of pyrite requires either dissolution of FeS or undersaturation of the pore fluids with respect to these minerals (RICKARD, 1975). Supersaturation in Mono Lake pore fluids is driven by high pH and sulfide levels. Humic acid is a minor sink of Fe in these sediments. The primary Fe reactions include the reductive dissolution of oxides in the lake waters and upper ten cm of sediment, and the precipitation of FeS. The reactivity of Fe to the acidic cation exchanger indicates that carbonate minerals may also be a secondary sink of Fe. However, this Fe may have been mobilized from other solids by proton exchange.

Manganese oxide dissolution is initiated below the chemocline, but there is no evidence of precipitation in this region. There is evidence of rapid precipitation directly across the sediment-water interface. Like Fe, Mn oxide reductive dissolution is greatest in the upper ten cm of sediment. Solubility calculations indicate that the lake bottom brines are undersaturated with respect to MnS. Directly below the sediment-water interface the pore fluids are supersaturated with respect to this mineral. These results suggest that a discrete MnS phase controls the solubility of this metal in Mono Lake sediments.

The extraction profiles for Cu, Zn, Pb, Co, and Cd are shown in Fig. 13. Copper was reactive to hydrogen peroxide. The greatest amount is extracted just below the sediment-water interface where 61% of the aqua regia extractable is recovered. This amount decreases to a relatively constant 20% at depth. In most horizons humic acid complexes account for 2 to 4% of the aqua regia extractable. In two horizons the complexed Cu accounted for 7 and 9.5% of the aqua regia extractable. The sequential extraction results and pore-fluid data for Cu suggest that a mobilization occurs in the top ten cm of sediment. The amount extracted is relatively constant below this horizon. The most likely reactions for Cu include release from dissolving oxides and algal debris and precipitation of a sulfide or humic acid complex. Since humic acid complexation is minor, sulfides represent the major sedimentary sink. The sequential extraction experiment cannot distinguish the type of sulfide forming.

Hydrogen peroxide extracts the most Zn in the upper 10 cm of sediment. Below 15 cm the relative reactivities of the acidic cation exchanger and the reducing and oxidizing solutions are similar. Reactivity to the neutral exchanger increases up to 9 cm after which it drops to a constant value. Reactivity to the acidic cation exchanger is also greatest in this region. The highest reactivity is in the upper 10 cm where 25% of the aqua regia extractable is recovered by sequential extraction solutions. Below this horizon the recovered amount is constant at values close to 10%. Humic acid complexes account for 3 to 5% of the aqua regia extractable Zn throughout the core.

The chemistry of Zn at Mono Lake is complicated. The metal is mobilized in the pore fluids of the upper few cm of sediment. The pore-fluid concentrations do not change below. The pore fluids are supersaturated with respect to Zn sulfides, unless some unknown ligands are complexing the metal in solution. Some of the peroxide extractable Zn in the upper 10 cm of sediment may be from organic matter of planktonic origin, but the extracted metal

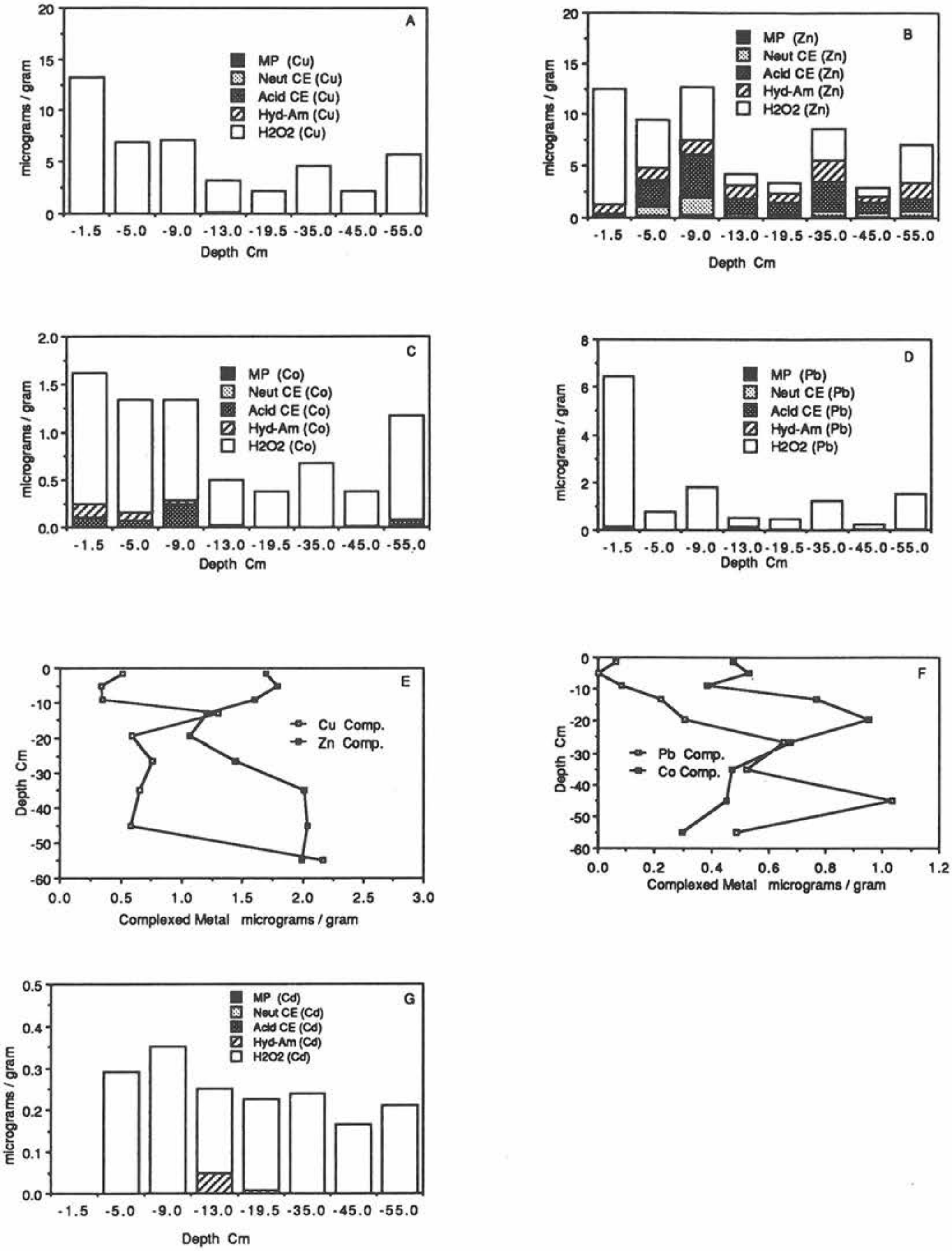


FIG. 13. Sequential and humic acid extraction results for Cu, Zn, Pb, Co, and Cd from Mono Lake sediments: a) Cu sequential extraction; The largest stack represents 46% of total sedimentary Cu; b) Zn sequential extraction; The largest stack represents 16% of total sedimentary Zn; c) Co sequential extraction; The largest stack represents 16% of total sedimentary Co; d) Pb sequential extraction; The largest stack represents 40% of total sedimentary Pb; e) Cu and Zn humic acid extractions; The greatest amount of complexed Cu is 7.5% of the total; The greatest amount of complexed Zn is 2.5% of the total; f) Co and Pb humic acid extractions; The greatest amount of complexed Pb is 6.5% of the total; The greatest amount of complexed Co is 9.5% of the total; g) Cd sequential extraction; Most stacks represent 100% of the aqua regia extractable Cd.

may also be from sulfides. There are other labile forms of Zn present. Reactivity to the reducing solution suggests adsorption onto metal oxides. The acidic cation exchanger is also effective, except at the top of the sedimentary column. The pathways of Zn diagenesis are difficult to elucidate from this data. A possible interpretation is the release of Zn from metal oxides and organic matter of planktonic origin in the bottom brines and upper 10 cm of sediment. The major sedimentary sink is some type of sulfide, either an authigenic Zn sulfide or coprecipitated with other sulfides.

Lead is extractable with the oxidizing solution. The greatest reactivity occurs just below the sediment-water interface. In this region 41% of the aqua regia extractable Pb was recovered. Below this horizon, the recoverable amount varies from 3 to 20%. Humic acid complexation increases in importance with depth. Near the sediment-water interface there is little complexed. The amount increases to 10% of the aqua regia extractable near the bottom of the core. The extraction profile for Pb is very similar to Cu with the greatest reactivity to the oxidizing solution occurring near the sediment-water interface. The extraction is releasing Pb from non-humic organic matter and sulfides. Extraction from sulfides may be dominant source of Pb. Lead is rapidly precipitated as there is no detectable metal in the pore fluids. Humic acid complexation of Pb increases with depth despite the fact that reactivity to extracting solutions decreases. The oxidizing solution, below 10 cm of the sediment-water interface, is probably extracting Pb from sulfides. The per cent of Pb extractable by sequential extraction is positively correlated to that of Fe which suggests that Pb may be involved in coprecipitation with Fe monosulfides.

The majority of reactive Co is released by the oxidizing solution, particularly in the upper 10 cm of core. There is also reactivity to the reducing solution and the acid cation exchanger in this region. Reactivity to the latter two reagents is largely absent below the 10 cm horizon except at the bottom of the core where the acid cation exchanger extracts a small amount. The highest percentage of aqua regia extractable metal, complexed to Mono Lake humic acid, is for Co. The complexes account for 10 to 25% of the aqua regia extractable Co. Cobalt has decreasing reactivity to the reducing solution in the upper 10 cm of core, which indicates that some metal is adsorbed on the dissolving metal oxides. The amount of humic acid bound Co increases down to the 10 cm horizon as adsorption onto metal oxides decreases in importance. The primary associations for Co are with organic matter and sulfides. It is not possible to tell if authigenic Co sulfides are forming, or if co-precipitation with Fe monosulfides occurs.

Cadmium is extractable with the oxidizing solution, but there was no evidence for complexation with humic acid. Its profile is unusual in that the metal was not extractable at the sediment-water interface but is very reactive below. The pore fluids are supersaturated with respect to the Cd sulfide phase greenockite. There is no correlation of Cd extraction chemistry with other elements. The precipitation of a discrete Cd sulfide phase probably occurs.

The sedimentary chemistry of Cu, Zn, Pb, and Co is affected by the following factors: 1) the reductive dissolution of Fe and Mn oxides, which is greatest in the upper ten cm of core; 2) the decomposition of organic material, which occurs throughout the core; 3) the high sulfide activity of the pore fluids; 4) the high pore-fluid pH; and 5) the presence of humic acid. The dissolution of Fe and Mn oxides results in the loss of major adsorbing phases for these elements. The extractability of these elements is greatest in the upper ten cm, where the oxides are undergoing active reductive dissolution. Some extractability of these elements may be due to the release of metals from algal debris in the initial stages of anaerobic decomposition. The majority of the extracted metals are probably from labile sulfides. The extraction profiles for Cu, Zn, Pb, Co, are similar to those for Fe and Mn which suggests a related sedimentary geochemistry. It is possible that coprecipitation with FeS occurs but this cannot be determined solely from the extraction data.

The extraction profiles for Mo and V are shown in Fig. 14. An extremely labile form of Mo is present throughout the core which is recovered with the first three extractions. A more refractory form of Mo is also present which is extracted by the oxidizing solution. Molybdenum is quantitatively recovered by the sequential extraction reagents. Molybdenum is also mobilized by sodium hydroxide, but there is no complexation with humic acid.

Vanadium is mobilized primarily by the reducing and oxidizing solutions. There is a minor amount of labile V which is released with distilled/de-ionized water and the neutral cation exchanger. There is no change throughout the sediments in the amount extracted by the reducing solution but the amount of peroxide extractable V increases with depth. In most core sections about 50% of the aqua regia extractable V is recovered by sequential extraction reagents. There is some V complexed to humic acid but the amount is very low, less than 1% of the aqua regia extractable.

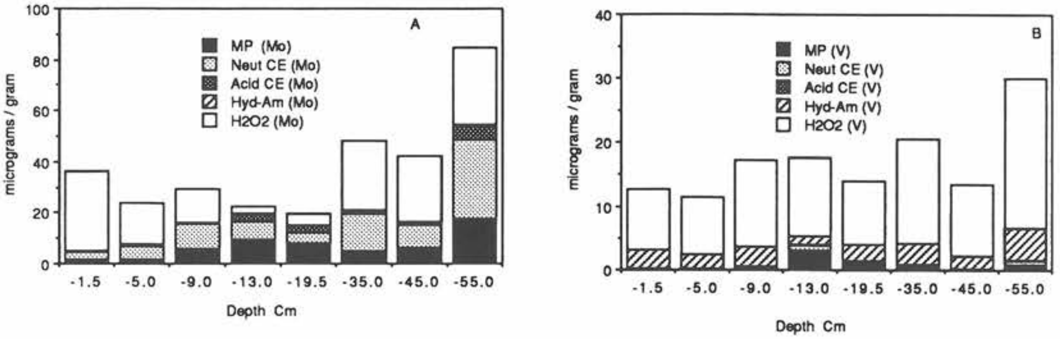


FIG. 14. Sequential extraction results for Mo and V from Mono Lake sediments: a) Mo; Most stacks represent 100% of total sedimentary Mo; b) V; Most stacks represent 45% of total sedimentary V.

There is no evidence of sedimentary re-distribution of V and Mo in Mono Lake sediments. Since reducing conditions occur throughout the sediments there is no chance for re-distribution. A gradient of oxidizing to reducing conditions is required. Vanadium is present in these sediments as the reduced oxycation, $V(OH)_2^+$, according to the pe and pH conditions. The oxycation will readily adsorb onto sedimentary particles or be complexed by organic matter. Molybdenum has been shown to be associated with sulfides in anoxic environments (VOLKOV and FOMINA, 1974; BERTINE, 1972). It has been suggested (BERTINE, 1972) that Mo co-precipitates with Fe monosulfides. Molybdenum is easily mobilized from anoxic sediments and is only immobile in the presence of sulfide. Molybdenum solubility is probably controlled by sulfide precipitation throughout Mono Lake sediments.

Mono Lake summary

Mono Lake is a saline alkaline lake, pH = 9.65, with anoxic bottom waters due to the presence, during 1985 and 1986, of a chemocline near 15 m of depth. The presence of an oxycline/chemocline results in the initiation of the reductive dissolution of Fe and Mn oxides and of sulfate reduction in the bottom brines. Maximum dissolution of labile sedimentary oxides (Fe, Mn) occurs in the top ten cm of sediment and refractory oxides are reduced below. Sulfide production occurs throughout the length of core in response to high total sedimentary organic carbon (5–7%), which is labile with respect to bacterial metabolism, and abundant sulfate. The Fe and Mn oxides are replaced primarily by metal sulfides following reductive dissolution.

Supersaturation with respect to Fe monosulfide is initiated in the water column. Across the sediment-water interface the degree of supersaturation increases and stabilizes at about 3 log units. The pore-fluid supersaturation with respect to Fe sulfide is driven by the positive sulfide gradient and the high pH, which is buffered above 9 for the length of the core. The lake water brines are not supersaturated with respect to MnS, but the pore fluids are. The Fe monosulfide minerals are metastable with respect to pyrite. Pyrite formation is inhibited because of the pore-fluid supersaturation with respect to Fe monosulfide.

Sequential extraction procedures tend to recover higher amounts of some trace metals from Mono Lake sediments relative to Walker Lake sediments. This is particularly the case for Fe, Zn, Cu, Co, and Pb (2 to 61% relative to the aqua regia extractable). This is probably related to the dissolution of Fe and Mn oxides in the upper part of the core and the precipitation of these elements into extractable phases. Manganese extractability was less from Mono Lake sediments relative to Walker Lake sediments (between 18 to 43% relative to the aqua regia extractable). This is probably related to the initiation of Mn oxide dissolution in the Mono Lake water column, as opposed to the sediments at Walker Lake, and its possible precipitation as an authigenic sulfide at Mono Lake. Similar to the situation at Walker Lake, Cd and Mo can be quantitatively extracted from Mono Lake sediments. The extraction of V is relatively constant in Mono Lake sediments because only one oxidation state is possible. Humic acids, although abundant in the Mono Lake sediments (8% of the TOC), are an insignificant sink of Fe and in general account for less than 1% of the aqua regia extractable. Cobalt is most reactive to humic acid complexation. Between 10 to 25% of the aqua regia extractable is complexed to humic acid. Copper is the next most reactive element. The greatest complexation of Cu by humic acid is close to 10% of the aqua regia extractable, but is closer to 2 to 4% in most core sections.

The group of elements Fe, Mn, Cu, Zn, Pb, and Co are related in the sense that their extraction profiles are similar. In all cases the greatest extractability occurs in the upper part of the core with a trend of constant reactivity below. These elements are associated with metal oxides, algal debris, and sulfides upon sedimentation and are released to the pore fluids as these phases are degraded. Sulfide phases are the dominant sink below 10 cm. The similarity of the extraction profiles suggests that co-precipitation with Fe monosulfides occurs but this would have to be proven by experimentation. An alterative interpretation is that this group of metals is mobilized during the peroxide extraction due to the generation of acid by oxidation of FeS. In this case the metals are not geochemically linked with FeS by co-precipitation, but rather, their geochemical mobility is linked to the oxidation of FeS. Manganese may be present as a discrete sulfide as suggested by the ion activity products and the extraction profiles. Cadmium probably also precipitates as a discrete sulfide, as suggested by the extraction results.

Molybdenum and V are not involved in diagenetic sedimentary re-distribution at Mono Lake as was the case at Walker Lake. This is due to the reducing conditions occurring throughout the sedimentary column and the anoxic bottom brines. There is no opportunity for these two elements to migrate along a redox gradient as at Walker Lake. Molybdenum precipitates as a sulfide. Vanadium is reduced to the oxycation species and is adsorbed onto organic matter and residual oxides. High levels of DOC, up to 150 mg/l, occur in the Mono Lake pore fluids. This material is a ligand for Cu, Fe, and Mn. The pore-fluid data suggests that it may also be a ligand for Co and V. This is indicated by the positive correlation among Co and V concentrations and the amount of DOC at the three sites.

The metal geochemistry at Mono Lake sediments is therefore dominated by the reductive dissolution of metal oxides in the top ten cm and metastable equilibrium with respect to Fe sulfide. Trace metals are extracted by the oxidizing solution which degrades the Fe monosulfides. Deeper cores are required to determine how and where metal stabilizing reactions occur.

Great Salt Lake brine chemistry

The Great Salt Lake is a meromictic hypersaline Na-Mg-Cl-SO_4 brine of low alkalinity. The major element water-column composition for site GSL3 is given in Table 7. The bottom waters have similar compositions but varying densities. The most concentrated brines occur in the North Basin. The ionic strength of the surface waters of the South Arm is close to 1.0. The ionic strength of the bottom waters of the North Basin of the South Arm is 4.5 whereas the South Basin bottom brines have an ionic strength of 3.0, and those of the South Basin deep site have an ionic strength of 3.6. These measurements were taken in September, 1986. All waters are undersaturated with respect to halite and gypsum but are close to saturation with aragonite (SPENCER *et al.,* 1985). Water column sulfate concentrations range from 3.5 to 13.9 g/l in the South Basin and from 3.4 to 20.2 g/l in the North Basin.

Table 7. Great Salt Lake water column. Composition at site GSL3. Samples collected 9-86 (STURM, 1986)

Depth (m)	Concentration (g/l)					
	Na^+	Mg^{2+}	K^+	Ca^{2+}	Cl^-	SO_4^{2-}
0.15	15.5	1.82	1.20	0.12	27.7	3.48
1.5	15.6	1.68	1.25	0.12	28.4	3.48
3.1	15.7	1.79	1.25	0.13	28.4	3.44
4.6	15.5	1.78	1.20	0.13	28.4	3.46
6.1	15.7	1.80	1.20	0.13	28.4	3.41
7.6	22.0	2.25	1.80	0.15	38.3	4.53
9.1	45.5	4.95	2.88	0.25	80.1	9.36
10.6	56.5	6.02	3.60	0.28	100.6	12.2
12.2	57.7	6.46	3.71	0.30	104.4	12.7
13.0	58.5	6.65	3.75	0.31	105.9	13.9

The maximum concentration of solutes related to microbiological activity and organic decomposition, such as alkalinity, DOC, and sulfide, are found in the bottom brines. These species tend to decrease in concentration across the sediment-water interface. The concentrations of these species are dependent upon the decomposition of organic matter by anaerobic processes with sulfate as the terminal electron acceptor. Fig. 15 shows the water column and pore-fluid concentration profiles for alkalinity, pH, DOC, and sulfide for 1986. Total alkalinity doubles in concentration from the surface to the bottom brines. The increase is due to sulfate and metal oxide reduction which consumes protons. Although total alkalinity increases, the pH of the water column decreases. This is due to the release of carbon dioxide and organic acids from decomposing organic matter. The profile of Fig. 15c suggests that there are no major alkalinity producing reactions in the sediments. The pH also decreases across the sediment-water interface. The values stabilize at 6.5 and 6.6 at the North and South Basin sites. Sulfide is not present in the surface brines.

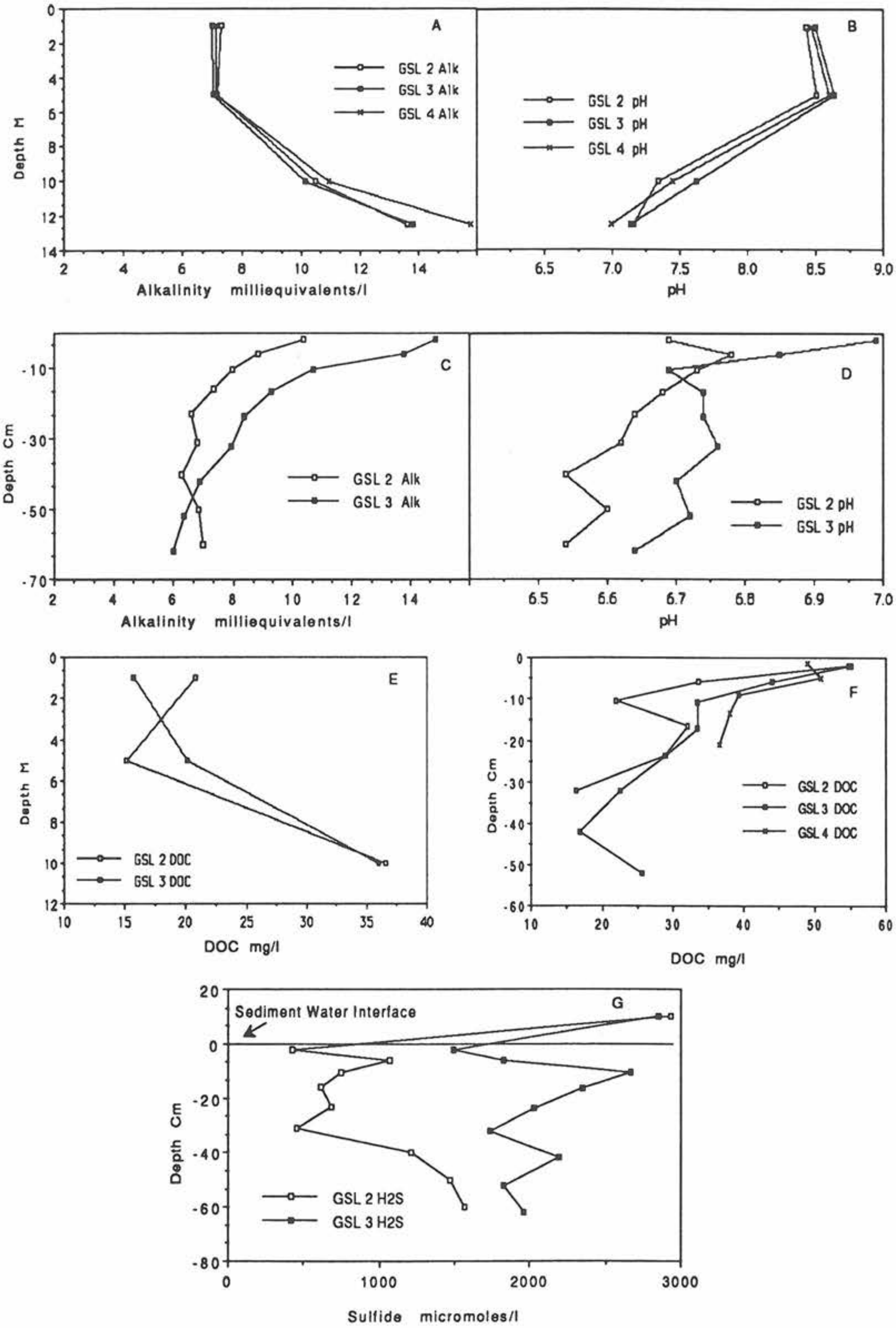


FIG. 15. Water column and pore-fluid geochemistry of Great Salt Lake: a) water column alkalinity; b) water column pH; c) pore-fluid alkalinity; d) pore-fluid pH; e) water column DOC; f) pore-fluid DOC; g) bottom brine and pore-fluid hydrogen sulfide.

The total sulfide bottom brine concentrations are close to 3 millimolar. H_2S is the major sulfide species below 10 m in the lake and throughout the pore fluids. The pe of the brines is just slightly more negative than −3.38 as calculated from the SO_4^{2-}/HS^- ratio and pH.

Pore-fluid sulfide concentrations are low relative to the bottom brines of the lake. The drop in concentration in the pore fluids is not due to Fe sulfide precipitation. The reductive dissolution of Fe oxides is greatest in the bottom brines of the lake and is of much less importance in the sediments. Sulfate is also not a limiting factor; pore fluids contain from 10 to 30 g SO_4^{2-}/l. Instead, sedimentary organic matter is refractory and degrades at a slower rate relative to the organic matter of the lake brines. The amount of organic carbon currently accumulating in Great Salt Lake sediments is lower than what would be expected for a productive lake with a shallow oxic mixolimnion and a reducing monimolimnion. The TOC of the surficial sediments is 2.5% for the South Basin site and 1.5% for the North Basin site. These concentrations decrease and stabilize at values between 1.0 to 1.1% for either site at 5 to 8 cm below the sediment-water interface. The data presented is consistent with an interpretation that planktonic organic matter is largely recycled to carbon dioxide within the anoxic water column. The mechanism is entrainment and decomposition of algal debris in the high density bottom brines. The process is most effective at the North Basin site which has the most dense fluids. The lowest accumulation of sedimentary organic carbon and the lowest pore-fluid sulfide concentrations occur there. Variations in DOC are also consistent with this interpretation. DOC can increase in concentration in anoxic environments from microbial metabolism of labile organic matter by sulfate reduction. DOC is highest in the lake brines and upper 5 to 10 cm of sediment but decreases in concentration below. Since the organic matter of the sediments degrades at a much lower rate, relative to the organic matter suspended in the bottom brines, DOC production and concentration are much lower in the pore fluids relative to the bottom brine.

Iron and Mn concentrations increase across the chemocline by reductive dissolution of the oxides. Fine-grained oxides of these two metals are also entrained in the bottom brines. Bisulfide ion is the most probable electron donor for reductive dissolution. The lake and pore-fluid profiles are shown in Fig. 16. The concentration profiles are similar to those for DOC. This is due, in part, to entrainment of metal oxide particles in the anoxic bottom brines where reductive dissolution occurs.

Precipitation reactions also affect Fe and Mn. Solubility calculations show that the bottom brines and pore fluids of the upper 10 cm of sediment are supersaturated with respect to mackinawite and pyrite (Fig. 16e). Precipitation of a FeS phase probably occurs in the bottom brines, which accumulates as a layer of black particles at the sediment-water interface. Pyrite forms below this zone and the mechanism of pyrite precipitation is discussed below. The waters are undersaturated with respect to all Mn sulfide phases by over two orders of magnitude and therefore no discrete MnS phases are precipitating.

The concentration profiles of most cationic trace metals show no definite trends. The water column and pore-fluid concentrations are given in Table 8. Dissolved Cu differs at the three sites with the concentrations either decreasing, increasing, or remaining more or less unchanged across the chemocline and sediment-water interface. The Cu pore-fluid concentrations do not vary significantly from those of the lake water. Lake water Zn concentrations also vary in different ways at the three sites. A concentration increase is noted in the upper few cm of sediment with decreasing concentrations below. Cobalt is present in the surface waters but is undetectable in the bottom brines suggesting that rapid precipitation occurs. Cobalt is undetectable in the upper 12 cm of sediment. A maximum concentration is observed near 17 cm with decreasing amounts below. Cadmium is not detected in the Great Salt Lake brines. Lead was analyzed by differential pulse anodic stripping voltammetry. A peak was detected for the surface brines which had the same half wave potential of the standard. The concentration was 2.5 micrograms/l. A peak, shifted by −150 mv, was detected in the bottom brine sample. The concentration was 15 micrograms/l. The shift in potential indicates that Pb is complexed by a strong ligand. These peaks completely disappear across the sediment-water interface indicating the absence of dissolved Pb.

Molybdenum concentrations decrease across the chemocline by a factor of 4 for both the North and South Basins. After a slight mobilization in the surficial pore fluids, Mo concentrations continue to decrease. Water column V concentrations show contrasting behavior in the North and South Basins. An increase with depth is observed in the North Basin and a decrease in the South. The South Basin pore-fluid concentrations are always higher than those of the North.

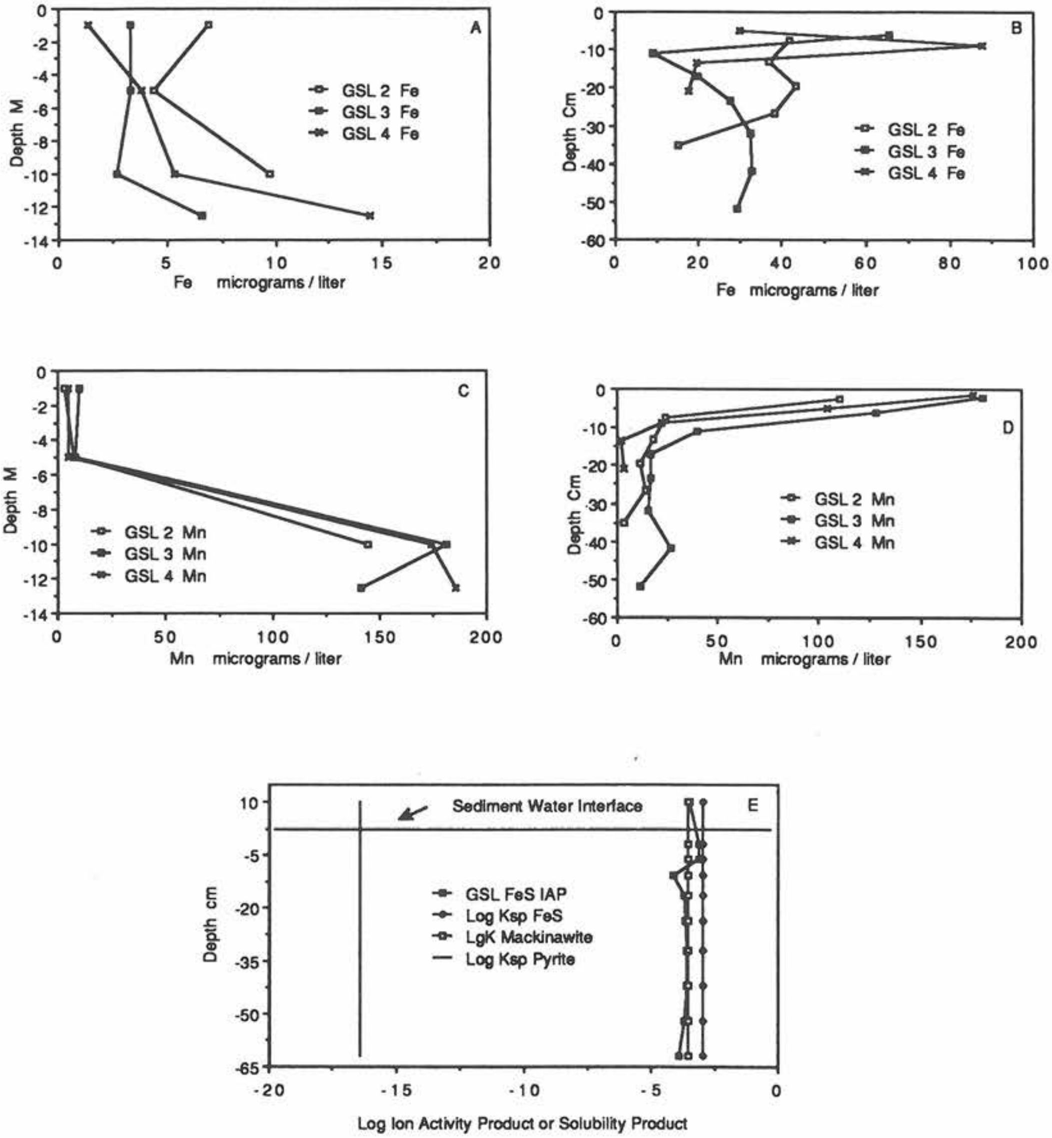


FIG. 16. Great Salt Lake water column and pore-fluid trace metal concentrations: a) water column Fe; b) pore-fluid Fe; c) water column Mn; d) pore-fluid Mn; e) water column and pore-fluid FeS ion activity products and saturation indices for amorphous FeS, mackinawite, and pyrite.

Great Salt Lake sedimentary chemistry

The mineralogy of Great Salt Lake sediments has been described by SPENCER (1982) and SPENCER *et al.* (1984) as part of their study on the lake level chronology of the Bonneville Basin. The sediments under study in this report were deposited after the fall from the Bonneville level about 13,000 years ago (SPENCER's, 1982, Unit 1). The sediments are pelleted sand. The mineralogy is quite uniform and consists of 15% quartz, 25% aragonite, 10% calcite, and up to 50% clay minerals. The clays are predominantly smectite. Minor amounts of feldspars and sulfides are present (SPENCER *et al.,* 1984). The sediments are black for the upper 5 cm and gray below. Iron monosulfides are responsible for the black color at the sediment-water interface.

The profiles for total sedimentary organic carbon are shown in Fig. 6. The surficial sediments contain the most organic carbon with the highest amounts in the South Basin. Both basins have similar amounts below 10 cm. Two horizons were analyzed

Table 8. Great Salt Lake water column and pore fluids. Dissolved trace metals

Depth	Cu	Zn	Co	Pb	Cd	Mo	V
Lake waters Depth: meters Metal concentration: micrograms/liter							
Site GSL2							
1.0	6.5	8.7	N.A.*	N.A.	N.A.	23.6	3.1
5.0	10.2	14.1	N.A.	N.A.	N.A.	27.8	3.8
10.0	3.2	21.1	N.A.	N.A.	N.A.	9.4	8.7
Site GSL3							
1.0	4.9	13.3	1.2	3.4	N.D.**	30.4	4.0
5.0	3.2	10.9	0.5	N.A.	N.D.	27.3	4.0
10.0	3.6	10.3	N.D.	10.0	N.D.	8.2	2.1
12.5	6.1	11.0	N.D.	12.5	N.D.	4.9	1.7
Site GSL4							
1.0	5.1	12.8	N.A.	N.A.	N.A.	N.A.	N.A.
5.0	3.7	8.0	N.A.	N.A.	N.A.	N.A.	N.A.
10.0	8.6	11.4	N.A.	N.A.	N.A.	N.A.	N.A.
12.5	10.4	18.9	N.A.	N.A.	N.A.	N.A.	N.A.
Pore fluids Depth: centimeters							
Site GSL2							
2.5	5.6	21.7	N.A.	N.A.	N.A.	7.6	1.2
7.5	5.5	20.0	N.A.	N.A.	N.A.	3.5	1.1
13.0	8.4	18.8	N.A.	N.A.	N.A.	3.9	0.8
19.5	10.5	19.8	N.A.	N.A.	N.A.	11.2	0.8
26.5	12.7	18.8	N.A.	N.A.	N.A.	3.7	1.4
35.0	5.6	14.9	N.A.	N.A.	N.A.	4.8	1.2
Site GSL 3							
2.0	9.7	32.0	N.D.	N.A.	N.A.	12.9	3.6
6.0	9.2	24.0	N.D.	N.D.	N.D.	9.9	1.5
11.0	5.9	22.3	N.D.	N.D.	N.D.	8.6	2.2
17.0	7.2	26.5	2.8	N.A.	N.A.	8.1	3.3
23.5	8.6	20.6	1.4	N.A.	N.A.	3.6	2.4
32.0	9.3	17.1	0.9	N.D.	N.D.	6.1	3.8
42.0	6.4	13.8	0.9	N.A.	N.A.	2.9	2.2
52.0	6.0	14.2	0.5	N.A.	N.A.	2.3	2.0

for humic acid concentrations (0 to 8 cm and 13 to 20 cm). Humic acids account for 0.7 and 4.3% of the TOC in these horizons.

The concentrations of total metals and aqua regia extractable metals are given in Table 9. There are no total metal analyses for the bottom brine particles due to the small sample size. Immediately apparent is the surface enrichment in Cu, Pb, Zn, Cd, and Mo. This is due to runoff from a large open pit Cu mine in the nearby Oquirrh Mountains. Despite the anthropogenic enrichment, the dissolved concentrations of these metals in the pore fluids are not unusually high. The pre-industrial total sedimentary concentrations of all metals are less than that of the average black shale except for Mo.

Great Salt Lake sequential and humic acid extractions

Sequential extractions of Great Salt Lake sediment included particles suspended in the bottom brines as well as the sedimentary material.

The sequential extraction profiles for Fe and Mn are shown in Figs. 17a and 17b. Iron is extractable from the particles suspended in the bottom brines by both the reducing and oxidizing solutions. The reactivity decreases considerably across the sediment-water interface, and the oxidizing solution is the only reagent which releases any Fe. Iron is not extractable below 5 cm. There is no humic acid complexed Fe in the upper 8 cm. Below this horizon, between 3.5 to 6 ppm of Fe are complexed, which accounts for, at most, 0.2% of the aqua regia extractable Fe.

The greatest amount of Mn is extractable from particles suspended in the bottom brines. The acidic cation exchanger extracts the most Mn followed by the reducing solution. The neutral cation exchanger

Table 9. Great Salt Lake sediments. Total extractable and total sedimentary metals

Depth (cm)	Fe	Mn	Cu	Zn	Pb	Co	Cd	Mo	V
Metal concentration: Micrograms/gram Core location: GSL3									
Total extractable metals									
L.P.*	3000	120	130	160	36	1.5	0.06	20.1	6.7
2.0	3330	180	180	110	110	2.5	3.4	29.4	12.5
6.0	4400	180	41	66	54	2.6	0.7	4.5	11.8
11.0	3600	210	7.1	27	3.4	1.7	0.02	3.9	11.4
17.0	4300	240	7.8	29	5.6	2.4	0.09	3.3	11.4
23.5	3900	250	7.1	29	4.3	2.2	0.02	2.3	10.8
32.0	3500	230	6.2	29	4.7	2.4	0.15	1.9	10.4
42.0	3800	220	7.5	25	3.6	2.3	0.10	1.5	11.5
52.0	2700	180	4.6	26	3.6	1.9	0.08	0.2	8.7
Total sedimentary metals									
2.5	11000	180	210	120	110	6.0	3.0	61.0	30
10.5	14000	240	24	67	14	6.0	<1	10.0	34
23.5	15000	280	11	54	6	6.0	<1	8.0	30
52.0	15000	250	11	59	6	6.0	<1	7.0	32

* L.P. refers to particles suspended in the bottom brines of the lake.

and hydrogen peroxide extract similar amounts. Nearly all of the aqua regia extractable Mn is recovered by these procedures. Across the sediment-water interface the reactivity is much less and hydrogen peroxide is the most efficient extractant, followed by the reducing solution. Below 5 cm of the sediment-water interface the reactivity does not change. Small amounts are released by the oxidizing and reducing solutions and the acidic cation exchanger. There is no Mn complexed to humic acid in these sediments.

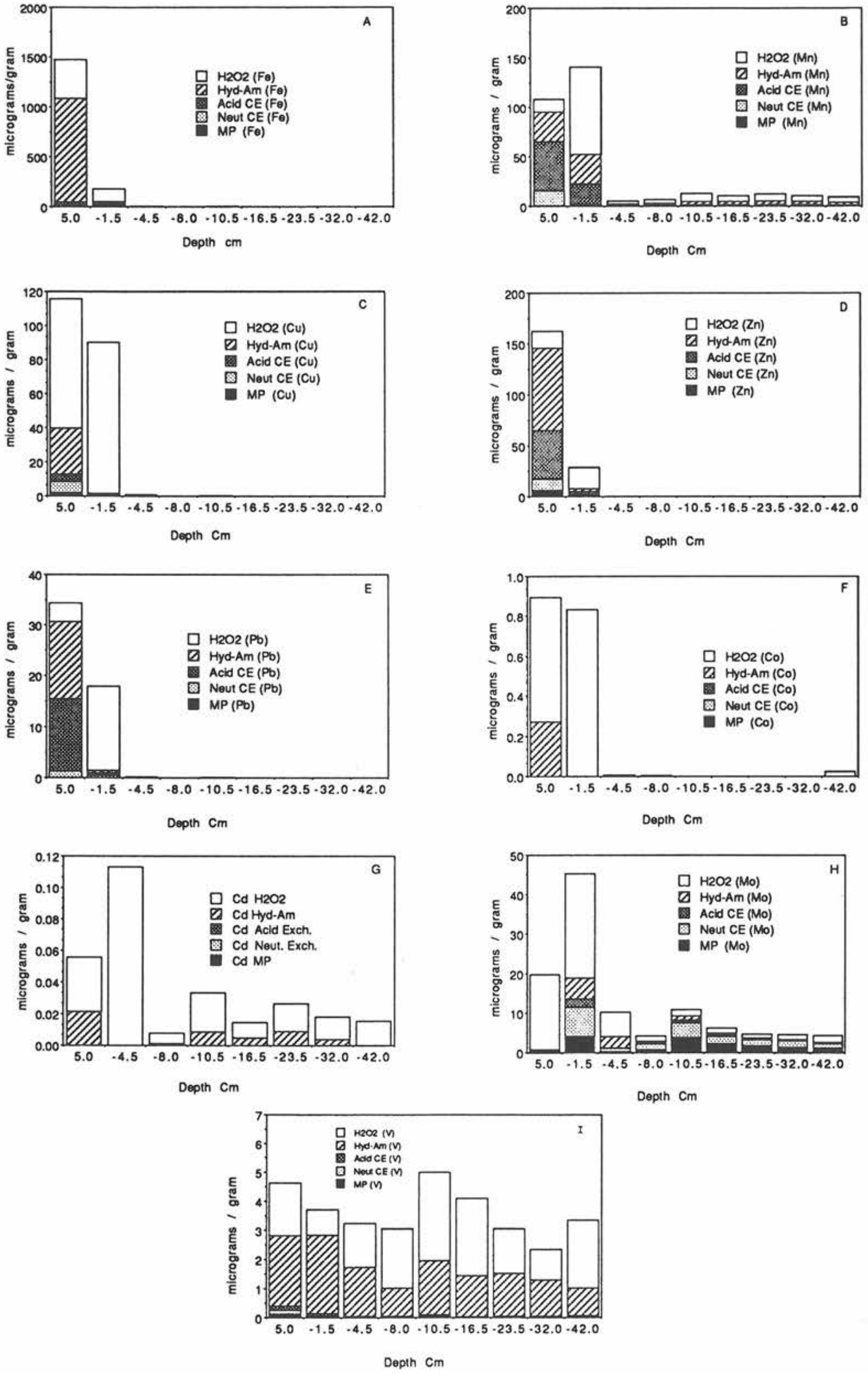
Manganese and Fe undergo reductive dissolution below the chemocline which results in a concentration increase of dissolved metals. The suspended metal oxides can be extracted by the reducing solution. The pore-fluid metal concentrations decrease with depth except for a mobilization of Fe in the top few cm. Of most significance is the reversal in reactivity across the sediment-water interface of solid phase Fe and Mn with respect to the extracting reagents. Up to 50% of the lake water particulate Fe and 90% of the Mn is extractable. This decreases to about 5% across the sediment-water interface. The Fe extracted from the surficial sediment is released by hydrogen peroxide and below this horizon there is no reactivity. The reactivity of Mn with respect to the sequential extraction procedures is constant at 5% of the aqua regia extractable below 5 cm of sediment.

It is inferred that sedimentary Fe is stabilized by the formation of pyrite. This is supported by SPENCER *et al.* (1984), who found that 50% of the sedimentary sulfur, in this interval, is pyritic. The formation of pyrite involves the following reactions in the water column and across the sediment-water interface: sulfate reduction producing sulfide ions; reduction of Fe oxides, by sulfide, to dissolved ferrous Fe; oxidation of sulfide ions by oxygen at the chemocline or by metal oxides in the bottom brines and sediments to provide elemental sulfur; reaction of the elemental sulfur with HS^- to provide polysulfides; precipitation of Fe monosulfide, and final production of pyrite by one of two mechanisms. Pyrite may form by direct precipitation following dissolution of the Fe monosulfide. Alternatively, the Fe monosulfide may react with residual oxide minerals to form greigite which would then alter to pyrite. These reactions have been described from experiments and field observations by BERNER (1970), RICKARD (1974, 1975), and PYZIK and SOMMER (1981) and were reviewed by MORSE *et al.* (1987). Direct precipitation, following the dissolution of Fe monosulfide, is probably the most important pathway for the Great Salt Lake. The critical requirement is the dissolution of the Fe monosulfide. The lake bottom brines are close to equilibrium with respect to mackinawite, but the pore fluids, below 10 cm of the sediment-water interface, are undersaturated. All other conditions for pyrite formation are ideal. Sulfate reduction occurs and elemental sulfur can form in the bottom brines, or at the sediment-water interface, by reaction of metal oxides with sulfide ions. The decrease in pore-fluid sulfide, dissolved Fe, and pH results in undersaturation of the pore fluids with respect to Fe monosulfides. While this occurs, all fluids are supersaturated with respect to pyrite. Direct precipitation of pyrite has been observed in salt marsh sediments where sulfate reduction is rapid, organic matter concentrations are high, and pH is low (HOWARTH, 1979; HOWARTH and TEAL, 1979; LUTHER *et al.*, 1982; GIBLIN and HOWARTH, 1984).

The water-column reactions are dominated by Fe monosulfide formation due to rapid kinetics and supersaturation. A decrease in pore-fluid pH and H_2S allows for the dissolution of FeS phases as the pore fluids become either undersaturated, or close to equilibrium, with respect to these minerals. The environment is also favorable for elemental sulfur production and the result is pyrite precipitation. The pyrite formation reactions go to completion in the upper 5 to 10 cm of sediment. This is indicated by the unreactivity of Fe to the extracting solutions below 5 cm and the change in sediment color from black to gray. Pyrite is not attacked by hydrogen peroxide but the metastable Fe sulfides are. These, and organic bound Fe in algal debris, account for the peroxide extractable Fe in the top 5 cm of sediment. Humic acid bound Fe is low at the Great Salt Lake. Maximum humic acid concentration occurs below the zone of pyrite formation. Pyrite is stable in anoxic sediments and therefore complexation is low.

The reactions for Mn are dissolution of oxides in the bottom brines and upper few cm of sediment, release from algal debris, and precipitation of a stable phase and an extractable phase. It has been shown that pyrite is capable of incorporating Mn into its structure (JACOBS *et al.*, 1985). These same authors showed that in low temperature marine systems metals do not appear to be in equilibrium with pure sulfide phases. It is proposed that this process also occurs at the Great Salt Lake and that it represents the major mechanism of Mn immobilization in Great Salt Lake sediments. There is a small amount of peroxide extractable Mn below 5 cm of the sediment-water interface. The solid phase association of peroxide extractable Mn cannot be inferred from these experiments.

The extraction profiles for Cu, Zn, Pb, Co, and


A
micrograms/gram
Depth cm
H2O2 (Fe)
Hyd-Am (Fe)
Acid CE (Fe)
Neut CE (Fe)
MP (Fe)
B
micrograms / gram
Depth Cm
H2O2 (Mn)
Hyd-Am (Mn)
Acid CE (Mn)
Neut CE (Mn)
MP (Mn)
C
H2O2 (Cu)
Hyd-Am (Cu)
Acid CE (Cu)
Neut CE (Cu)
MP (Cu)
D
H2O2 (Zn)
Hyd-Am (Zn)
Acid CE (Zn)
Neut CE (Zn)
MP (Zn)
E
H2O2 (Pb)
Hyd-Am (Pb)
Acid CE (Pb)
Neut CE (Pb)
MP (Pb)
F
H2O2 (Co)
Hyd-Am (Co)
Acid CE (Co)
Neut CE (Co)
MP (Co)
G
Cd H2O2
Cd Hyd-Am
Cd Acid Exch.
Cd Neut. Exch.
Cd MP
H
H2O2 (Mo)
Hyd-Am (Mo)
Acid CE (Mo)
Neut CE (Mo)
MP (Mo)
I
H2O2 (V)
Hyd-Am (V)
Acid CE (V)
Neut CE (V)
MP (V)
5.0 -1.5 -4.5 -8.0 -10.5 -16.5 -23.5 -32.0 -42.0

Cd are shown in Figs. 17c–17g. The shape of the profiles for Cu, Zn, Pb, and Cd are affected by the anthropogenic enrichment at the sediment-water interface. The greatest quantity of Cu, Zn, Pb, and Co, relative to the aqua regia extractable, is recovered from particles suspended in the bottom brines. Hydrogen peroxide and the reducing solution are most effective for Cu and Co. The reducing solution and the acidic cation exchanger are most effective for Zn and Pb. Most of the aqua regia extractable metals are recovered in this region. Across the sediment-water interface the reactivity changes. There is a small residual reactivity to hydrogen peroxide near the sediment-water interface. Below this horizon the particles are not reactive to the sequential extraction procedures.

Copper is the most reactive metal to humic acid complexation in these sediments. Below 10 cm of sediment, 4.5% of the aqua regia extractable Cu is complexed. Between 0 and 10 cm, 1 to 2% is complexed. There is a small amount of Zn which is complexed, but the amount is always well below 1% of the aqua regia extractable. No Pb or Co is complexed by humic acid.

Most of the aqua regia extractable Cd is recovered from the bottom brine particles by the oxidizing solution. There is also slight reactivity to the reducing solution. Most of the sedimentary Cd is extractable by hydrogen peroxide. No Cd is complexed to humic acid.

The elements Fe, Mn, Cu, Zn, Pb, and Co have similar reactivity to sequential extraction reagents. It is inferred that the trace elements are stabilized by pyrite formation. These elements may also have been associated with the Fe monosulfide precursors, and this association is preserved during conversion of the monosulfide to pyrite. The result is a significant decrease in reactivity across the sediment-water interface. The most compelling evidence for the co-precipitation of these elements with pyrite is provided by the sequential extraction data.

The bottom brine solid phase association of Cu, Zn, Pb, Co, and Cd can be with either metal oxides, organic matter, and sulfides. This is suggested by the high reactivity to both the reducing and oxidizing solutions. The oxides and labile organic matter are largely destroyed in the bottom brines and surficial sediments. The small reactivity of these elements at the sediment-water interface is probably due to their association with Fe monosulfide prior to pyrite formation.

Humic acids are an insignificant sink of trace metals because pyrite forms above the horizon of maximum humic acid concentration. Only Cu has any appreciable reactivity to the Great Salt Lake humic acids. The incorporation of the trace metals into pyrite is apparently an extremely stable configuration and prevents organic complexation from taking place.

Cadmium chemistry at Great Salt Lake is different from the other metals. Only a small amount of Cd is associated with metal oxides in the bottom brines and sediments. BENJAMIN and LECKIE (1981) showed that pH levels above 8 are required for quantitative removal of Cd from solution by adsorption onto Fe oxide. Therefore, adsorption should occur in the surface brines, but desorption should occur below the chemocline. The only extracting reagent which is effective for Cd is the oxidizing solution. There are several core horizons where Cd recovery is 100% of the aqua regia extractable. Cadmium can be extracted with hydrogen peroxide while iron cannot. Thus, Cd is probably not co-precipitated with pyrite, but instead precipitates as a discrete sulfide phase.

The extraction profiles for Mo and V are shown in Figs. 17h and 17i. Molybdenum is highly reactive to sequential extraction reagents throughout the core. The Mo associated with water column particles is most reactive to hydrogen peroxide. Molybdenum of the surficial sediments is also extractable with hydrogen peroxide but a significant residual fraction is also present. Below 5 cm of the sediment-water interface, a labile fraction is present which is extractable with distilled/de-ionized water and the neutral cation exchanger. There is also a hydrogen peroxide extractable fraction present. The only residual Mo was found in the surficial sediments. It has already been demonstrated (Table 9) that these sediments are enriched in Mo due to runoff from an open pit Cu mine. The residual Mo in this region may be present in stable phases from this run-off. There is no Mo complexed by humic acid in these sediments.

FIG. 17. Sequential extraction results for Fe, Mn, Cu, Zn, Pb, Co, Cd, Mo, and V from Great Salt Lake sediments: a) Fe; The largest stack represents 50% of aqua regia extractable Fe; b) Mn; The largest stack represents 77% of total sedimentary Mn; c) Cu; The largest stack represents 86% of aqua regia extractable Cu; d) Zn; The largest stack represents 94% of aqua regia extractable Zn; e) Pb; The largest stack represents 96% of aqua regia extractable Pb; f) Co; The largest stack represents 60% of aqua regia extractable Co; g) Cd; Most stacks represent 100% of total sedimentary Cd; h) Mo; The largest stack represents 75% of total sedimentary Mo.; Other stacks represent 60 to 100% of the total; i) V; Most stacks represent 14.7% of total sedimentary V.

The data for Mo suggests that precipitation of a discrete Mo sulfide phase occurs in the bottom lake brines and surficial sediments. As discussed, Mo is associated with Fe monosulfides in anoxic waters but is released during the transformation to pyrite (KOROLOV, 1958). BERTINE (1972) showed for anoxic marine systems that 70% of the sedimentary Mo is associated with Fe sulfides. Bertine suggested that precipitation of a discrete Mo sulfide occurs. The data for this study shows that Mo is removed from solution below the chemocline. In this region Mo is taken out of solution as either a discrete Mo sulfide or adsorbed onto the surface of Fe monosulfide. Adsorption onto metal oxides is unlikely since reductive dissolution is taking place. There is a slight increase in dissolved Mo just below the sediment-water interface with decreasing concentrations below. This mobilization is probably due to the release of Mo from the surface of Fe monosulfide minerals which are dissolving in this region. The extraction of Mo from the water column particles is accomplished with hydrogen peroxide but none of this material is associated with organic matter, as indicated by gel permeation chromatography, which suggests that the metal is being released from sulfides. Sedimentary Mo is highly labile and can be extracted quantitatively below 5 cm of sediment with a variety of reagents including hydrogen peroxide. Molybdenum can be extracted with hydrogen peroxide whereas iron cannot. Thus, there is no association of Mo with pyrite. The data supports the concept of a discrete Mo sulfide.

Vanadium reactivity is quite constant below the sediment-water interface. The water column particles are more reactive than the sediments but have less total V. Reactivity to the reducing solution and hydrogen peroxide is similar. About 75% of the aqua regia extractable V is recovered from the water column particles whereas 25 to 45% of the aqua regia extractable is recovered from the sedimentary column. There is no V complexed by humic acid in these sediments.

The extraction of V is dominated by the reducing and oxidizing solutions and there is no change in reactivity throughout the core. The hydrogen peroxide extractable form of V may be an organic complex. According to the Eh-pH diagram of HEM (1977) the V species, consistent with the conditions at the Great Salt Lake bottom waters and pore fluids, should be $V(OH)_2^+$. This species can be complexed by organic matter.

The chemistry of Mo and V in Great Salt Lake are considerably different. Only 40 to 50% of the aqua regia extractable V is labile to sequential extraction solutions, whereas Mo is quantitatively extractable. Only the reducing and oxidizing solutions are effective for V whereas for Mo the milder reagents, such as distilled water and the neutral cation exchanger, are also effective. Vanadium is therefore present in more stable forms relative to Mo. Although the peroxide extractable form of V is probably an organic complex, the form extracted by the reducing solution is unknown.

Great Salt Lake summary

At the Great Salt Lake a combination of physical, chemical, and biological factors result in the stabilization of the metals Fe, Mn, Cu, Zn, Pb, and Co, by pyrite formation, in the bottom brines and upper few cm of sediment. Fine-grained material, such as algal debris and metal oxides, are entrained in the dense bottom brines. Here, organic matter degradation, sulfide production, and metal oxide reductive dissolution are greatest. Associated trace metals are released from the metal oxides and precipitate in some sulfide phase. The drop in pH across the chemocline is due to the release of carbon dioxide from decaying organic matter and poor buffering of the brine. The pH continues to drop across the sediment-water interface. Sulfide concentrations are lower in the pore fluids relative to the lake and as a result Fe monosulfide dissolves and is replaced by pyrite. This reaction goes to completion in a narrow zone just below the sediment-water interface. The geochemical conditions are such that euhedral pyrite is expected to form by direct precipitation following the dissolution of Fe monosulfide. Pyrite is formed from ferrous Fe, sulfide, and polysulfide ions. The low alkalinity helps this process by allowing pH to drop in concert with falling sulfide levels.

The selective extraction results indicate that Mn, Zn, Cu, Pb, and Co co-precipitate with Fe in pyrite whereas Mo and Cd form discrete sulfides. Vanadium is most likely present as an oxycation which is complexed to organic matter or adsorbed onto sedimentary material. Furthermore, maximum humic acid production occurs below the region of pyrite formation and as a result the Great Salt Lake humic acids have extremely low trace metal content.

Two conclusions can be drawn for the Great Salt Lake system. The first is that pyrite formation and the co-precipitation of Mn, Cu, Zn, Pb, and Co result in the immobilization of this group along with Fe. This group of metals is extremely unreactive to the sequential extraction solutions and therefore is expected to be resistant to any further mobilization during diagenesis unless a change in pore-fluid chemistry occurs which is capable of dissolving pyrite. Although Mo and Cd precipitate as sulfides, they are extractable. This indicates that they do not co-precipitate with pyrite, but are subject to mobilization, particularly by oxidizing fluids. Molybdenum appears to be immobile only in the presence of dissolved sulfide. Vanadium can also be mobilized by oxidizing conditions, particularly if it undergoes an oxidation state change to the oxyanion or if the organic matter to which it is complexed is degraded. The second conclusion is that despite high surface water algal productivity, a relatively narrow oxygenated zone of lake waters, and intensely reducing bottom brines, the accumulation of organic carbon in Great Salt Lake sediments is not very high with concentrations barely above 1% by weight. A stratified water column with very dense bottom brines and high sulfate concentrations results in the recycling of organic carbon to carbon dioxide in the water column with low sedimentary accumulation. The degradation of algal debris in the bottom brine is rapid since the reactions are not limited by diffusion of fresh oxidant to the algal surfaces and the concentration of sulfate is very high. Therefore surface productivity is not the only consideration in predicting the accumulation of organic carbon in sedimentary basins. Physical and chemical factors of the water column are important. This study shows that organic carbon can be effectively mineralized to carbon dioxide in an anoxic stratified system if an excess of sulfate is present.

CONCLUSIONS AND SUMMARY

Local conditions and brine composition impact the chemistry of trace metals associated with reactive particles such as metal oxides and organic matter in closed basin lakes. Brine composition and concentration affect: 1) the stratification of the water column, which defines a sharp redox transition and may also affect the sedimentation rate of fine-grained particles; 2) the sulfate concentration, which affects anaerobic organic matter degradation, sulfide production, and metal sulfide precipitation; 3) the total alkalinity, which affects buffering capacity and pH; 4) the location of organic matter degradation and the oxidants involved, which affects pH, alkalinity, sulfide and DOC concentrations; and 5) the location of the reductive dissolution of metal oxides, which affects trace metal adsorption. The lakes of this study are in different phases of brine evolution and the effects of two distinct brine types (alkaline and non-alkaline) on trace metal geochemistry were observed. The geochemistry of trace metals is affected by these compositional differences. The early diagenesis of trace metals in these three

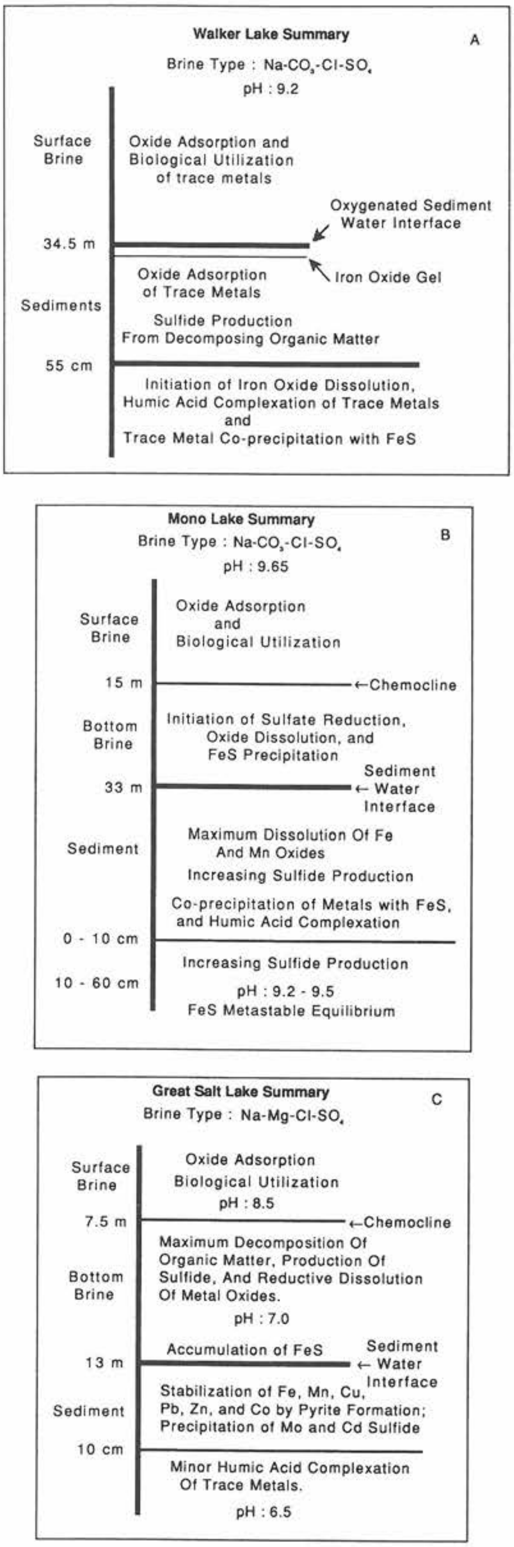


FIG. 18. Schematic representation of trace metal diagenesis: a) Walker Lake; b) Mono Lake; c) Great Salt Lake.

lakes is shown schematically in Figs. 18a, 18b and 18c. A chemically stratified water column at Mono and Great Salt Lakes results in the initiation of the reductive dissolution of Fe and Mn oxides in the bottom brines. This reaction goes to completion in the water column at the Great Salt Lake due to high brine density which results in the entrainment of metal oxides. At Mono Lake, reductive dissolution of Fe and Mn oxides is of greatest importance in the upper ten cm of sediment due to rapid deposition. The reductive dissolution of metal oxides and the release of trace metals occurs in a deeper sedimentary horizon at Walker Lake in as much as the water column is not stratified and oxygen reaches the bottom sediments. Differences in sulfide concentrations in the alkaline lake sediments result in different relative proportions of metal sulfide precipitation and humic acid complexation. Lower sulfide concentrations at Walker Lake result in a much higher amount of humic acid complexation of trace metals, relative to Mono Lake. This occurs in spite of higher sedimentary organic carbon and humic acid concentrations at Mono Lake. It was shown (DOMAGALSKI, 1988) that the structure of humic acids in both Walker and Mono Lakes is favorable for trace metal complexation. The dependence of trace metal geochemistry on brine composition and brine evolution suggests that the solid phase association of metals will be highly variable over long time frames. Brine chemistry can change rapidly in these lakes due to changes in inflow and climate. Stratification of the water column is a transient phenomenon. The stratification of Mono Lake has already broken down and trace metal geochemistry will adjust to an oxygenated sediment-water interface. Trace metal geochemistry will therefore only rarely assume steady state conditions.

One of the major differences between alkaline and non-alkaline lakes, as determined by this study, is the type of authigenic Fe sulfide minerals forming in the lake waters and sediment. The pH profiles and Fe sulfide activity products for the three lakes are shown in Fig. 19. Pyrite is prevented from forming during early diagenesis in the alkaline lakes due to supersaturation of the brines with respect to Fe monosulfide. This assumes that Fe monosulfide formation is favored, kinetically, over that of pyrite. The subsequent formation of pyrite requires dissolution of Fe monosulfide (RICKARD, 1975). Supersaturation with respect to Fe monosulfide is caused by high pH, due to buffered alkaline brines, and high sulfide concentrations. All other factors for pyrite formation are ideal. At the Great Salt Lake, poor buffering capacity of the brine results in a pH drop of two units from the surface waters to pore fluids. The drop in pH is driven by degradation of organic matter. Sedimentary pyrite forms rapidly at the Great Salt Lake due to decreasing pore-fluid pH and sulfide concentrations which lead to the dissolution of Fe monosulfides which precipitated in the bottom brines of the lake. The metastable Fe monosulfides persist in the upper meter of Mono and Walker Lake sediments.

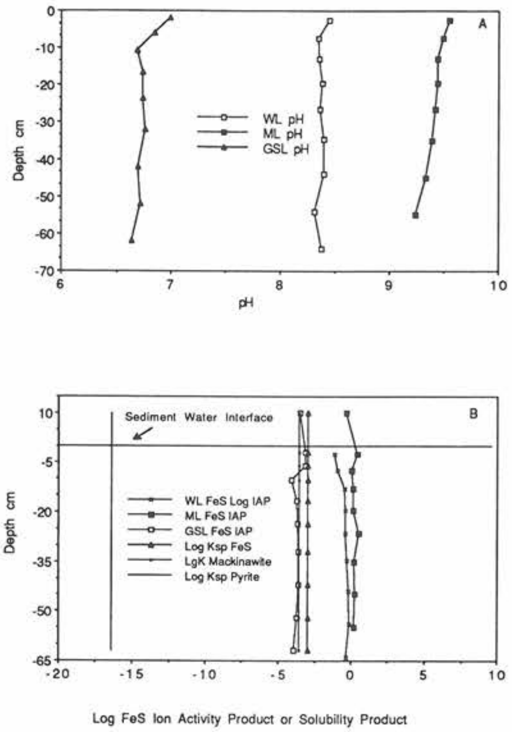


FIG. 19. Inter-basinal comparison of pore-fluid pH and FeS ion activity products: a) pH comparison; b) FeS ion activity product comparison.

Iron sulfide chemistry has an important impact on the trace metals Mn, Cu, Pb, Zn, and Co. These elements have zero to very low extractability from Great Salt Lake sediments due to co-precipitation with pyrite. They will only be mobilized, during diagenesis, by the dissolution of this stable phase. This requires oxidation. In contrast, these metals are highly extractable from Mono Lake sediments, particularly with hydrogen peroxide. Metal mobilization, to form an ore-forming fluid, can occur in alkaline sediments by a change in pore-fluid chemistry resulting in the degradation of FeS. The mobilization of cationic trace metals does not require oxidation if trace metals co-precipitate with FeS. Decreases in either sulfide concentration or pH allow for FeS dissolution. If sedimentary conditions for pyrite formation are not appropriate, following the dissolution of FeS, organic matter may be an important sink of Fe and those metals associated with the monosulfide. Pyrite formation requires the presence of elemental sulfur (BERNER, 1970). Elemental sulfur may be generated by oxidation of bisulfide if suitable oxidants, such as metal oxides, are available (PYZIK and SOMMER, 1981). Alternatively, FeS was shown to be easily oxidized and this reaction can contribute acidity to an ore-forming fluid, thereby increasing the solubility of cationic metals. EUGSTER (1985) suggested that alkaline basins may be potential sites of ore-forming processes. He proposed that metals can be transported as hydroxy complexes in the high pH environment and classified such deposits as the Green River Type. This work shows that metals, in alkaline sediments, are not present in stable phases during early diagenesis. Mobilization of metals, to form an ore-forming fluid, is therefore possible under the right set of conditions.

Pyrite formation, during early diagenesis in marine and non-marine systems, has been discussed by BERNER (1984) and reviewed by MORSE *et al.* (1987). Pyrite in marine sediments frequently has a framboidal texture which has been linked to a series of reactions involving Fe monosulfide and greigite precursors (SWEENEY and KAPLAN, 1973). The rapid formation of pyrite in salt marshes has been reported by HOWARTH (1979). The rapid precipitation of pyrite in salt marshes is attributed to conditions which favor undersaturation of Fe monosulfides. The Great Salt Lake, and systems like it, with highly dense bottom brines represents a unique pyrite forming environment. The bottom brine, with high sulfate, Fe oxide, and organic matter is a favorable environment for Fe monosulfide formation. Reactive organic matter is degraded and Fe minerals are reduced in the bottom brines. The Fe monosulfide dissolves directly across the sediment water interface and is replaced by pyrite. The locations of Fe monosulfide and pyrite precipitation are, therefore, separate. Although pyrite textures were not identified in this study, the conditions are right for the formation of euhedral crystals.

The geochemistry of Mo and V involves redox chemistry, precipitation of Mo sulfide, and adsorption of reduced V species onto metal oxides or sedimentary organic matter. Diagenetic mobilization of these two elements occurs at Walker Lake due to the presence of a diffuse redox transition zone within the sediments. In contrast, a sharp redox gradient occurs at the chemocline in meromictic systems and prevents any chance of sedimentary diagenetic re-distribution from occurring.

The Mono Lake brines and sediments provide an excellent natural laboratory for the study of low temperature metal-ligand interactions. The ligands include high molecular weight organic acids and also inorganic species. In particular, polysulfide ions should be abundant in the pore fluids due to high pH conditions which favor their production. Future work for trace metals should be directed towards the study of dissolved organic ligands, polysulfide ligands, the surface chemistry of Fe monosulfide minerals, and the metal sulfide mineralogy in deeper sedimentary sections. Future work at Walker Lake should be directed at comparing the effects of high and low pore-fluid sulfate concentrations on trace metal-organic carbon interactions and Fe sulfide mineralogy in deeper sedimentary horizons than those of this study. The two sites described in this study are ideal for this type of investigation.

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